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# The Production of Vat Dyes on Piece Goods

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A WORKS I have in mind has during the last eighteen months engaged no less than seven foremen vat dyers, and while this is probably an extreme case, it is very true to state that most firms experience difficulties in obtaining complete satisfaction with this class of work.

The importance of actual fast colors appears to be gradually becoming understood by the public, and people are now sufficiently educated in the matter to actually insist that they are buying guaranteed work. "Garment replaced if color fades" has perhaps become a standard inscription to all goods that will in their normal life be subjected to some form of deteriorative treatment, be it the action of the sun or the weekly wash-day. Probably at least ninety-five per cent of the shirtings, overalls and casements now produced are done in fast colors, that is to say in the generally accepted sense of the word, reasonably fast that after a normal treatment they will appear to the owner very much the same as when originally purchased.

It would be dangerous to prophesy whether vat dyestuffs will eventually be ousted by azoic colors, but whether this be the case or not, or some superior range of dyestuffs be discovered, the problems and difficulties of vat dyeing will surely remain long enough to trouble most of us.

The process of vat dyeing is certainly more than ordinarily difficult and this review is not by any means intended as an exhaustive article on the subject, but more as a brief survey of some of the practical difficulties experienced in nine years controlling a vat dyehouse.

**EDITOR'S NOTE: This article was written in England and consequently many of the products mentioned and terms used are English. Persons wishing to do so may obtain the names of similar products from domestic distributors.**

### General Methods of Jig Dyeing

Whereas we are offered various machines for the dyeing of cops or yarn, a piece goods dyer is practically confined to an everyday dye jig. Here, so far as I can see, no particularly interesting or novel ideas have recently been suggested.

A jig, therefore, constitutes practically the only machine used in dyeing piece goods. For vat dyeing, the jig must be as near perfect working order as possible. It is of extreme importance that all rollers are in perfect working order, and there is no danger of any creasing after the goods have been running a matter of say twenty ends. The process of vat dyeing is comparatively slow and tedious and one cannot consider attempting to dye a round of vats, with fear that the goods may start "piling" or running unevenly. Such faults are usually due to some guide roller that is untrue, or some such mechanical fault.

Wood and iron jigs are largely used, but preference should certainly be given to jigs lined with monel metal, vitralite, coralite or some such compound, if only for the ease with which they may be cleaned out. Jigs nowadays are mostly supplied with friction clutches, thereby eliminating a jerky start, subjecting delicate cloths to considerable tension. Copper as a metal should never be used for any part of a vat dye jig.

### Working from Standard Solutions

For very pale shades, where little actual dyestuff is used, it is often the practice to work from a freshly made standard of the vat dye.

The following represents a very simple recipe used to produce a pale ecru shade:

2-5 pieces. Weight, 210 pounds. Length, 120 yards. Mercerized Poplins. Shade, Ecru 4.

*Yellow Standard—*

8 ozs. Indanthren Yellow 3R
12 ozs. hydrosulfite powder
1 gill caustic soda 76° Tw.

1 gal.

*Brown Standard—*

8 ozs. Caledon Brown RS
12 ozs. hydrosulfite powder
1 gill caustic soda 76° Tw.

1 gal.

5 pints Brown Standard
3 pints Yellow Standard (divided)
1 lb.-1 hydrosulfite
2 pints caustic soda 76° Tw.
2 pints oleine
1 lb. Nekal BX dry

in approximately 30 gallons; 4 ends; usual "finish-off." Dyeing temperature, 50° C.

The cloth is run on the dye jig through a weak warm soda ash bath, and is then ready for dyeing. It seems quite a common practice to give the goods two ends through hydrosulfite and caustic soda at 50° C., before entering the actual dye liquor. The idea lying behind this method is that so-called "air-bubbles" will otherwise interfere with a level dyeing. Whether this be the case or not, the writer has never found the extra two ends beneficial. The standards may be strained before use, and while this is certainly a precaution against color specking, it is not an essential.

The color is divided equally over the first two ends, taking special care that sufficient time has been allowed between adding the standard to the dye jig and commencing running. In the case illustrated probably two to three minutes is quite long enough to ensure obtaining a proper vat. The process is again repeated before commencing the second end. Once the color and hydrosulfite have been added, special care must be taken in seeing that the temperature is not on any account allowed to rise above 50° C., and attention must be given to this point. A common fault is to turn on the steam, take a reading and find that the temperature has risen above that advocated for dyeing, and then allow to cool down. The damage has already been done with some dyestuffs, and they may partially have decomposed, likewise the hydrosulfite. This is frequently the cause of "out-of-solutions," and a mistake in this direction cannot often be passed off. Two ends are then given in the cooling liquor, probably in the case of such a pale shade, without the addition of any Glauber's salt. During the fourth passage through the liquor, the batches are stopped for a moment, and the jigger cuts a small pattern out for shading purposes.

Mention may be made here of the also important point that once vat dyeing is commenced, the goods must never be left at a standstill between the ends. The strings or cords should be untied immediately and the batches allowed to swing round. This does not mean to say that one can leave the batches for long in this state—once started, vat dyeing must be carried right through to a finish. There is no knocking off for lunch or dinner at this game.

**Production of Heavy Shades**

When I speak of the many difficulties of obtaining satisfaction with vat dyed goods, I think these may be more confined to heavier shades, such as are at the moment popular in the casement trade—shades ranging between 5 and 20%. Here rather a somewhat different procedure has to be adopted.

Obviously, in the first place, a standard solution of the dyestuff could not possibly be made up, and the raw color has simply to be added to the jig itself.

The following represent a few typical working recipes, taken from standard batches:

1-4 pieces. Weight, 130 pounds. Length, 90 yards. Mercerized Brocades. Shade, Nigger.

12 lbs. Indanthren Brown BR
1 lb. Paradone Yellow G
2 lbs.-2 lbs. hydrosulfite
3 pints caustic soda 76° Tw.
1 lb. Nekal BX dry
5 lbs.-5 lbs. Glauber's salt.

in approximately 30 gallons; 8 ends; usual "finish-off." Dyeing temperature, 50°C.

2-3 pieces. Weight, 210 pounds. Length, 100 yards. Artificial Silk Brocs. Shade, Blue 210.

15 lbs. Caledon Blue RCS
1 lb. Caledon Violet RS
1½ lbs.-1½ lbs. hydrosulfite
4 pints caustic soda 76° Tw.
1 lb. Nekal BX dry

in approximately 30 gallons; 6 ends; usual "finish-off." Dyeing temperature, 45° C.

The principle is essentially the same as before, but we are dealing with a large weight of dyestuffs, and difficulties may very easily arise. The following are some of the main points to watch:

(1) Relation of liquor to weight of material.
(2) Relation of liquor to weight of dyestuff.
(3) Correct vatting of the dyestuff.
(4) Obtaining complete exhaustion.
(5) Obtaining shade required without various additions of color.

(1) Twenty-five gallons of water per batch of 120 lbs. serves as a useful guide, but much depends upon the nature of the cloth being dealt with. Obviously a batch of a low plain cloth will not appear anything like as bulky as the same weight of a very spongy heavily brocaded cloth, and less liquor will probably be needed. It is far better to have too much liquor than too little. Shortage of water is the main cause of batches appearing "endy" and too much liquor will tend to retard exhaustion. A happy medium must be chosen.

(2) I know not off hand of any experiments having ever been conducted with regard to actually saturated or super-saturated solutions of vat dyestuffs, but sufficient is to say that it would be extremely dangerous to ever commence dyeing anywhere near this border line, and precautions must be taken to ensure that the dyestuff is perfectly in solution throughout the runnings. It would

be absurd to ever commence dyeing with a vat of fifteen gallons and fifty pounds of dyestuff. The question is one for individual consideration, and no hard and fast rules can be laid down.

(3) The art of vatting the colors and maintaining the dyestuff in solution throughout the dyeing is perhaps the most important point of all connected with vat dyeing, particularly evident when dyeing with heavy shades.

According to official instructions issued, the caustic soda is first added to the bath at the temperature required, then the requisite amount of hydrosulfite strewn in, while stirring slowly. Finally the dyestuff, previously mixed with ten times the amount of water, (is passed in through a fine sieve), stirring slowly, until in about ten minutes the solution is complete and dyeing may be commenced.

As will be discussed later, the proportion of caustic soda and the correct dyeing temperature depends upon the particular class to which the dyestuff belongs. Dyers would do well to study the helpful information given us in this respect by our dyestuff manufacturers, and the individual characteristics of particular colors.

Never on any account commence dyeing unless you are absolutely certain beyond a shadow of doubt that every particle of dyestuff is in solution. Jiggers paid by piece work somewhat naturally tend to commence running before a proper vat has been formed—A procedure with extremely dangerous consequences.

(4) With direct colors, the cost of the dyestuff is almost negligible, but when dealing with vats, often powder colors, such as Indanthren Red FBB powder, the color cost is vital. Complete exhaustion, therefore, or as near as ever it is possible to obtain, must be aimed at.

Fortunately, with the dyestuffs we are discussing, this question of exhaustion is not a difficulty often met with. Judicious additions of Glauber's salt is often the main control of this point. Another factor which seems to play rather an important part in obtaining complete exhaustion is ensuring a thorough scouring of the cloth and the suitable addition of wetting-out agents. Some cloths appear to act almost akin to glass in their resistance to pick up the color, while others are just the very reverse and will mop up the dyestuff like a blotting pad. The addition of oleine or some sulfonated castor oil or one of such a wide range of products as are now on the market is useful when dealing with a tightly woven cloth, or a particularly highly twisted yarn.

(5) Disregarding for the moment the production effected by obtaining the requisite shade in four, six or eight ends, it is of extreme importance from a cost point of view that various additions of color are not necessary before obtaining the required shade. Firstly, with each addition of dyestuff, it is important to add also a certain amount of hydrosulfite and caustic soda, the former being quite an expensive assistant. More important, however, is the point that further additions of color do not seem to give the increase in shade that one would expect. By this I mean to say that if we already have 5 lbs. Indanthren Orange RRTS on 100 lbs. of cloth and are just a fraction on the thin side, it will require the addition of a further 2 lbs. to produce the shade that would be obtained using only 6 lbs. in the first instance. This is a point to always bear in mind when repeating shades that have previously only been obtained by various additions of color. Do not bunch together the whole of the color used when previously dyed, or the goods will be gloriously too heavy and some happy hours are ahead attempting to strip down! Apparently the explanation of this depends somehow on the dyebath becoming choked with hydrosulfite, certainly retarding in some way the affinity of the dye for the material.

When dealing with particularly heavy shades, such as navy blues, niggers and the like, one can almost appear to reach the stage where the addition of further dyestuff is useless and no apparent increase in depth can be noted. The best way here appears that if more color must be given, then it is best to knock off the existing liquor and get up a fresh dyebath entirely. Though perhaps appearing a somewhat expensive procedure, this is often the cheapest in the long run.

Considering therefore the above, it is certainly an enormous advantage if the required shade can be produced by first time pitching. Almost any one can obtain a required shade eventually, gradually creeping up to the tone and depth required, with perhaps half a dozen "weigh-outs." On the other hand, a dyer can make no worse mistake than pitching on the full side, with goods coming up too heavy. The question is of course to a great extent a matter purely of experience, but with careful mounting up of all possible pitches, it should not be very long before he has a comprehensive range of shades, more or less covering the whole of the normal field. Should the works be confined to one or two classes of goods, as is usually the case, then the dyer should not require such an enormous number of different pitches. With a collection of round about eight hundred, almost any required shade can be spotted or one near enough that only a trival alteration be necessary.

This system of first-time pitching is very satisfactory, providing a few points are carefully watched. For example, I divide my pitches as far as possible according to the different cloths. Thus, it would never be good policy to use a pitch on a brocade cloth for the production of a similar shade on a cotton slub or repp, even for the same weight of material. The same weight of dyestuff on the same weight of two different cloths will produce totally different depths of shade, and to a certain extent a difference in tone.

When dealing with viscose/cotton brocades, it is necessary to always note roughly the percentage of rayon. Again, it would certainly produce a different shade to use a pitch on a cloth containing a large percentage of viscose for a dyeing where the reverse were the case.

Never keep a pitch unless you are absolutely certain that it is quite correct, and finally, if in any doubt, such

as working with a new cloth, always keep the color on the lower side rather than the other extreme.

### Patterns for Shading Up

It is necessary to have some convenience fitted in the dyehouse for oxidizing and soaping "bits." Two small wooden becks, say measuring about two feet square, fitted with small steam pipes will serve the purpose. Ordinary pegs tied to strings are allowed to hang alongside these tanks, and jiggers' bits may be easily and conveniently thrown into the tank of boiling soap.

It is of course not by any means an easy matter to guarantee that these patterns will be absolutely representative of the pieces in hand, but they are the dyer's only guide, and every precaution need be taken to ensure such is the case. The length of time for instance left in perborate and soap should correspond as near as possible to what the goods will receive. It is difficult to calculate the length of time the pieces are in contact with boiling soap, since the passage through the liquor will in itself be only a matter of a few seconds. Three minutes in the perborate tank and five minutes in the boiling soap will certainly ensure the maximum result, and in the majority of cases, be about what the goods will receive. Bits should afterwards be mangled through a small hand mangle and dried on a covered steam pipe. When perfectly dry, allow to cool off very thoroughly, preferably by holding at some open window, and they are then ready for passing to the dyer for shading purposes.

### "Finishing-Off"

"Finishing-Off" is a term meaning the runnings after leaving the dye liquor proper. Briefly, it embodies washing-off, some form of oxidation and final soaping. The first point does not require much explanation. After letting off the dye liquor, two ends are given through fresh cold water.

There are two methods of oxidation usually carried out: (a) With the use of bichromate of soda and (b) Using sodium perborate. In the former case, the practise is to work at a strength of ⅛-¼ oz. per gallon along with the addition of about 3 pints acetic acid per 25 gallons of water. Some dyers work this cold, but the usual practise is to run at a temperature of about 50°C. Two ends are all that are usually needed to ensure complete oxidation, but at least two waters washing off are necessary before entering the boiling soap. Using the perborate of soda method, two ends are given at 50°C, 1½ lbs. each end being all that is required for the average shades. Colors that are very difficult to oxidize, such as Indanthren Brown BR will probably require three ends or a rather large dose of perborate. Perborate of soda must always be used for blues and greens, since no matter what concentration of bichromate of soda be employed, with all the soaping in the world, the true or accepted true shade of the dyestuff will never be obtained.

Comparing, therefore, the two methods of oxidation, the chief disadvantage with bichromate lies in the fact that at least two waters-off are essential before entering the soap. Considering an end as taking ten to fifteen minutes, which is often the case, it is rather an expensive job from a labor point of view. On the other hand, using perborate of soda, we are dealing with a product about eight times as expensive, but possessing the delightful advantage that one can enter the soap bath without any washing-off whatsoever and no danger of any over oxidation. So far as cost of labor and materials is concerned, there seems little to choose between the two. Personally, I always use perborate of soda.

The process of soaping is the final stage of our vat dyeing, and one that should not present many difficulties. A good soap is usually the cheapest and worked absolutely at the boil, at a strength of about ½ oz. per gallon, two ends will be all that is normally required. Certain dyestuffs unquestionably require more soaping than others, and it is of course rather important that the dyer satisfies himself that the goods are completely developed, before a final wash and away to another department.

The writer is at the moment conducting bulk trials with regard to the possibilities of oxidation and soaping in one bath. The production of soaps stable in acid solution tend to render this line of research more practicable, and in view of the present tedious methods employed, one cannot afford to ignore any possibilities that even offer a suspicion of saving.

The topping of vat colors with directs is a sacred subject rarely discussed amongst dyers and certainly never seen in print. My reputation is at stake, but I will go so far as to say that very few dyers fall short of this practice, and providing it is carried out within reason, I think it is perfectly permissible and can certainly not produce any inferior results. Certainly only a very limited amount of direct color should be used and one's choice of same should be limited to only the very fastest. An odd gill of Oxyphenine G standard or some such color cannot possibly be detected on heavy shades, and an occasional "spot" or direct color often makes all the difference between right and wrong. I do not in any way wish to encourage the practice, but the standard of matching now demanded is so very high that this liberty must surely be permitted.

### Change in Finish

A few useful words may be added here in pointing out the fact that goods are not necessarily required dead on shade when they leave the dyehouse, but are most definitely required on shade when they reach the warehouse. Every practical man knows only too well how shades seem to alter in finishing, and speaking from experience, it is heart breaking to know that goods have left you apparently very good matches, only for them to be rejected by the customer. The alteration in tone on standing and finishing can only be ascertained with experience. Each particular dyestuff seems to have its own little characteristics. Blue R.C.S. will redden up enormously after

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# The Evaluation of Textile Penetrants:

## An Improved Centrifugal Method*

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### Introduction

THE recent wide use of a variety of synthetic organic chemical products, as assistants in the penetration of textile fibers by liquids, has led to a considerable interest in the quantitative evaluation of the efficiency of these substances. The penetration of textile fibers is assisted by two classes of materials, solvents which remove the obstructions to penetration, and surface-active materials which greatly reduce the tension at interfaces and act as colloidal penetrating assistants: this paper will be concerned only with the surface-active materials. The action of solvent penetration assistants in aiding in the entrance of solutions into fibers requires no discussion, but the action of the colloidal penetrants is complicated by a number of factors which require study. No attempt is made to throw light on the mechanism of the action of penetrants, but a method for the practical evaluation of surface-active, or colloidal, textile penetrants is described.

It is necessary to examine a system in which the textile fiber, surrounded by oils and waxes together with a layer of sorbed gases, is in contact with a solution of the penetration assistant. If the solution is to penetrate the fiber it must displace this gas, emulsify the waxes and oils sufficiently to gain access to the material, and diffuse throughout the fiber by means of capillary forces. The evaluation of a penetration assistant is an evaluation, directly or indirectly, of the following factors:

(1) The tension of the solution at the interface liquid-adsorbed gas, as well as of the tension at the interface liquid-solid (fiber).

(2) The emulsifying action of the solution on the waxes and oils of the fiber.

A number of methods for the evaluation of textile penetration assistants have been reported in the literature but many are obviously only capable of giving a qualitative measure while others are limited through their failure to measure all of the factors involved. The methods may be divided roughly into three groups:

(1) Measurements of the forces acting at the surface of the solutions.

(2) Determinations of the time taken for a substance to wet-out and sink in a solution.

(3) Measurement of the quantity of liquid absorbed during a given period of time by the fiber.

Kind and Auerbach[7] made comparisons of wetting agents by measuring the drop number of solutions of the assistants. Herbig and Seyferth[6] made observations of the capillary rise in threads of yarn suspended under standard conditions in solutions of the wetting assistants: Auerbach[1] used as a method of evaluation the measure of the time required for a square of fabric floating on the surface of the liquid to become wet-out and sink. Ristenpart and Petzold[9] measured the time required for a submerged strand of the fiber to become sufficiently wet-out to sink, while Draves and Clarkson[2] measured the time required for a submerged skein to become sufficiently wet-out to sink when attached to a 1.5 gram weight. Herbig and Seyferth[4, 5] wet out yarn and centrifuged it under standard conditions in order to obtain a measure of the amount of water absorbed. Seck and Lachmann[10] immersed a weighed piece of cloth in a solution for a definite time, and after draining calculated the amount of solution absorbed from the gain in weight of the cloth.

Comparisons of wetting-assistants based on determinations of the surface tension of their solutions do not take into consideration the interfacial tension and the forces of capillary attraction involved. Methods based on the capillary rise in a thread digging into a solution of the assistant are stated by Herbig and Seyferth[6] to lead to conclusions contradictory to observations made in actual commercial practice. Methods which involve sinking-time measurements are frequently erratic in their performance since they depend upon the interface liquid-adsorbed gas, the behavior of which may be readily influenced both by the temperature and the viscosity of the solution. A method involving the use of a centrifuge to remove extraneous solution from the wet fibers appears much more likely to give uniformly reproducible results than does a method which relies upon the draining of the liquid from the fabric.

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*Analytical Edition, Nov. 15, Industrial & Engineering Chemistry.

The method of Herbig and Seyferth[4, 5] has certain defects which tend to render questionable any conclusions of a quantitative nature based on its use. Stöcker[11] has pointed out that large errors are introduced as a result of the procedure employed by Herbig because of the relatively long time interval between the wetting of the yarn and the subsequent centrifuging process. He also states that Herbig's immersion time is too short to give results of any significance. The work reported in this paper has eliminated the source of error pointed out by Stöcker, placed the method on a sound basis, and established a method of testing that will be of significance in industrial problems.

The primary function of any good textile penetration assistant is the production of a thorough and rapid penetration of fibers by a solution. It is of importance in the evaluation of textile penetration assistants to know the actual degree of saturation of the fiber with a solution, i.e., the extent to which the solution has penetrated into the fiber, at various time intervals during the wetting-out process, as well as to know the moisture content of a fiber when it is wet-out. These data, together with stability data, are those needed to evaluate the worth of penetration assistants.

### Outline of Method

Textile penetration assistants are most widely used in the processing of cotton. Most of the work with the centrifugal method has been confined to a study of cotton yarn. However, the method is applicable to other vegetable and to animal fibers. The cotton fiber used was in the form of skeins prepared from unbleached, unboiled out cotton yarn (40/2) of the type which is extensively used in the testing of dyestuffs. This yarn contained moisture which had been absorbed from the atmosphere, but several months' experience indicated that the validity of the results was not seriously impaired by the initial quantity of moisture present in the air-dry yarn provided the yarn was of uniform quality.

A skein of the raw cotton yarn, approximately 5 grams in weight, was weighed to the nearest centigram. The yarn was pulled tight several times in order to line up the strands, then doubled to form a loop of half the original length, and attached to an anchor. The skein was cut open at the top of the loop by means of shears and struck on the palm of the hand 8 to 10 times in order to separate and free the individual strands. This preparation produces uniformity in the physical condition of the skeins, while the shearing of the yarn facilitates the rapid expulsion of adsorbed air by the solution as it penetrates the fibers. The skein and anchor were dropped into a cylinder containing a solution of the penetration assistant at a known concentration. The yarn was immersed in this solution for a time, measured on a stop-watch graduated to read to fifths of a second, and was then transferred to the slowly revolving basket of a centrifuge by pouring the entire contents of the cylinder into the basket. The centrifuge used was a hand machine with a gear ratio of 1:36 and a basket radius of 5.5 centimeters. Since the time of contact of the yarn with the liquid is an important factor in this test, care was taken that the skein dropped from the cylinder into the basket with a variation of only a few fifths of a second from the desired wetting-out time. Within one second after the transfer of the skein, the speed of the slowly rotating basket was brought to approximately 2,160 R.P.M. and the extraneous solution was removed. The basket was revolved at this velocity for the desired time and then stopped quickly by means of a braking force. The skein was removed, detached from the anchor, and weighed in a weighing bottle. The quantity of solution retained by the yarn was expressed in terms of the initial weight of the skein.

The amount of solution in the yarn after this treatment is indicative of the amount of water absorbed. The percentage of moisture absorbed is a relative figure which depends entirely upon the length of the wetting-out time and the conditions employed in the centrifuging procedure. For this reason it is necessary to adopt a standard procedure that will give results which can be reproduced with reasonable accuracy and which at the same time will remove a minimum quantity of the solution actually absorbed by the fibers. To study the various conditions which can be employed and to select a proper testing procedure, a series of tests were made with solutions of Alkanol B, a commercial alkylated naphthalene sodium sulfonate, over a range of concentrations with a variation in the immersion time of from 15 to 60 seconds and in the centrifuging time of from 10 to 30 seconds. Five determinations were made at each concentration for each specified variation. A summary of the data is given in Table I.

**Table I**

**Penetration Tests on Cotton with Alkanol B Solutions in Water at 25° C.**

| Immersion Time, sec. | | 60 | 30 | 30 | 15 | 15 |
|---|---|---|---|---|---|---|
| Centrifuging Time, sec. | | 30 | 30 | 10 | 30 | 15 |
| Conc. g/1 | 0.0 | 27.4% | 21.1% | 24.6% | | |
| | 0.1 | 29.6 | 29.5 | 27.5 | 23.5% | 25.6% |
| | 0.2 | 36.1 | 34.0 | 33.1 | 29.8 | 29.5 |
| | 0.5 | 50.1 | 45.0 | 48.9 | 38.1 | 41.5 |
| | 1.0 | 64.9 | 55.8 | 68.8 | 50.1 | 53.2 |
| | 2.0 | 68.3 | 64.0 | 80.3 | 62.5 | 71.7 |
| | 3.0 | 65.1 | 66.1 | 86.2 | 67.4 | 78.2 |
| | 5.0 | 69.9 | 66.1 | 88.3 | 72.4 | 82.7 |

As a result of the above tests a standard wetting time of 15 seconds and a standard centrifuging time of 15 seconds was adopted. The immersion time of 15 seconds is sufficiently long for a good wetting agent to show pronounced activity at concentrations ordinarily used in commercial practice while the results obtained by centrifuging the yarn for 15 seconds are sufficiently reproducible to permit a definite distinction to be made in the activity of the solutions at different concentrations of the penetration assistant. To illustrate the variation to be expected be-

tween individual determinations, detailed information on experiments at four different concentrations of Alkanol B is given in Table II.

**Table II**

**Penetration Tests with Solutions of Alkanol B in Water at 25° C.**

| | | | | | | |
|---|---|---|---|---|---|---|
| Concentration 1.0 gram per liter | | | | | | |
| Trial No. | 1 | 2 | 3 | 4 | 5 | Average |
| Wt. Skein g. | 5.05 | 5.00 | 5.09 | 5.07 | 5.11 | |
| Wt. Water Absorbed, g. | 2.59 | 2.71 | 2.64 | 2.73 | 2.80 | |
| % Water Absorbed | 51.3 | 54.2 | 51.9 | 53.8 | 54.7 | 53.2 |
| Concentration 2.0 grams per liter | | | | | | |
| Trial No. | 1 | 2 | 3 | 4 | 5 | Average |
| Wt. Skein g. | 5.11 | 5.09 | 5.19 | 5.11 | 5.15 | |
| Wt. Water Absorbed, g. | 3.53 | 3.89 | 3.79 | 3.48 | 3.71 | |
| % Water Absorbed | 69.1 | 76.4 | 73.0 | 68.1 | 72.0 | 71.7 |
| Concentration 3.0 grams per liter | | | | | | |
| Trial No. | 1 | 2 | 3 | 4 | 5 | Average |
| Wt. Skein g. | 5.04 | 5.11 | 5.11 | 4.97 | 5.10 | |
| Wt. Water Absorbed, g. | 3.67 | 3.71 | 4.22 | 4.03 | 4.18 | |
| % Water Absorbed | 72.8 | 72.6 | 82.6 | 81.1 | 81.9 | 78.2 |
| Concentration 5.0 grams per liter | | | | | | |
| Trial No. | 1 | 2 | 3 | 4 | 5 | Average |
| Wt. Skein g. | 5.15 | 5.14 | 5.11 | 5.08 | 5.00 | |
| Wt. Water Absorbed, g. | 4.45 | 4.00 | 4.37 | 4.32 | 3.95 | |
| % Water Absorbed | 86.4 | 77.9 | 85.4 | 85.0 | 79.0 | 82.7 |

While the individual determinations of a given series in Table II show considerable variation, the mean averages obtained represent reasonably accurate evaluations of the quantity of solution retained by the cotton fibers. The probable error in the mean average of a series has been determined by the equation (1) where $\Sigma d^2$ is the sum of

$$(1) \qquad \text{P.E.} = 0.6745 \sqrt{\frac{\Sigma d^2}{n(n-1)}}$$

the squares of the deviations of the single observations from the mean. It was found that the probable error in the mean average was in each case less than 1.5%. The results are represented graphically in Figure I with logarithms of the concentrations plotted as abscissae and logarithms of the average per cent absorption plotted as ordinates. It is observed that a smooth curve can be drawn through the points plotted.

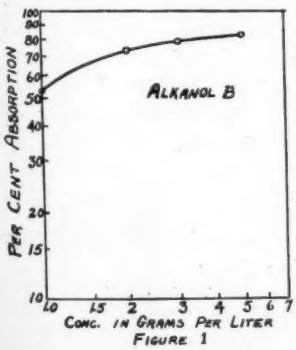

Figure 1

**Application of Method**

The method was applied to a study of a variety of chemical types of penetration assistants which represent the most important commercial products on the market at present.

Alkanol B is a di-alkylated naphthalene sodium sulfonate of 85.25% strength.

Gardinol WA Double Powder is a sodium lauryl sulfate product of 71.1% strength prepared from technical lauryl alcohol.

Gardinol CA Powder is a sodium oleyl sulfate product of 48.4% strength prepared from technical oleyl alcohol of iodine number 50.

Product D is a well known commercial material.

The soap used was a sodium oleate soap containing 79.4% of fatty acid salts.

**Penetration Efficiency of Water Solutions**

Tests of the wetting-out efficiency of solutions of these products were made over a range of concentrations at 25°C., 49°C. and 93°C.

A summary of the results obtained is given in Tables III, IV and V while graphical representations of the data in Tables III and IV are given in Figures 2 and 3. Each value given in these tables represents an average of five experimental determinations.

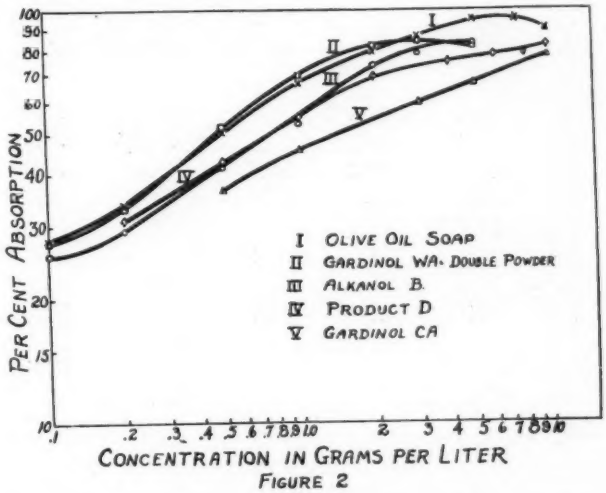

Figure 2

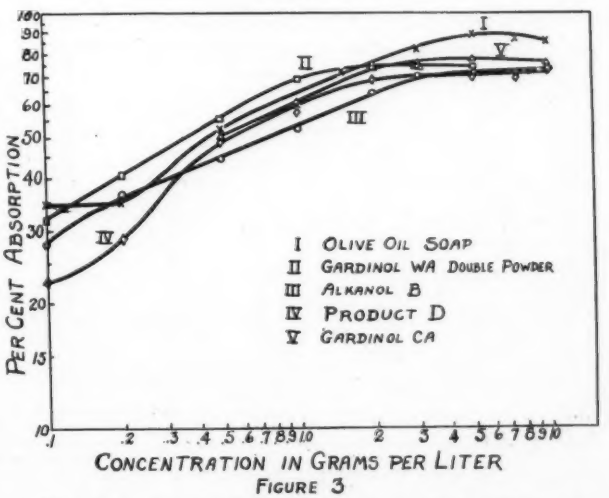

Figure 3

The data given in Tables III-V show that, with the exception of solutions of Gardinol CA Powder, the actual efficiency of the solutions of wetting-out agents studied decreases with increase in temperature. The results indicate that the surface activity of these solutions decreases as the temperature increases and this decrease in surface activity leads to the conclusion that these colloidal penetration assistants pass into molecular solution as the temperature is increased. On the other hand solutions of Gardinol CA Powder are shown to exhibit decidedly superior penetrating qualities at the higher temperatures. Solu-

tions of Gardinol CA Powder are particularly effective at 49°C. but still show some superiority even at 93°C. Lenher[8] has shown that the micelles of Gardinol CA Powder are too large to produce their maximum effect at 25°C. A dispersion of the micelles at higher temperatures into more effective sizes would account for the marked increase noted in the surface activity and the resultant penetration of the fiber by the solution.

**Table III**

**Water Absorbed by Cotton Yarn at 25° C. from Solutions of Textile Penetration Assistants**

| *Conc. g/l* | *Alkanol B* | *Gardinol WA Double Powder* | *Gardinol CA Powder* | *Product D* | *Soap* |
|---|---|---|---|---|---|
| 0.0 | 24.0% | | | | |
| 0.1 | 25.6 | 27.4% | | | 27.9% |
| 0.2 | 29.5 | 33.2 | | 30.9% | 33.6 |
| 0.5 | 41.5 | 52.2 | 36.3% | 43.1 | 50.8 |
| 1.0 | 53.2 | 69.1 | 45.6 | 55.0 | 66.4 |
| 2.0 | 71.7 | 81.2 | | 68.7 | 79.5 |
| 3.0 | 78.2 | 83.6 | 59.4 | | 85.2 |
| 4.0 | | | | 74.8 | |
| 5.0 | 82.7 | 81.5 | 66.1 | | 94.1 |
| 6.0 | | | | 78.0 | |
| 7.5 | | | | | 94.7 |
| 8.0 | | | | 79.4 | |
| 10.0 | | | 77.9 | 82.0 | 90.7 |

**Table IV**

**Water Absorbed by Cotton Yarn at 49° C. from Solutions of Textile Penetration Assistants**

| *Conc. g/l* | *Alkanol B* | *Gardinol WA Double Powder* | *Gardinol CA Powder* | *Product D* | *Soap* |
|---|---|---|---|---|---|
| 0.0 | 20.9% | 23.1% | | 19.2% | 25.5% |
| 0.1 | 27.8 | 31.9 | | 22.5 | 34.3 |
| 0.2 | 36.3 | 40.6 | | 28.8 | 35.0 |
| 0.5 | 44.2 | 55.6 | 50.8% | 48.7 | 52.1 |
| 1.0 | 52.6 | 68.9 | 61.0 | 57.4 | 60.1 |
| 1.5 | | | | | 72.0 |
| 2.0 | 64.0 | 73.1 | 73.9 | 69.0 | 73.9 |
| 3.0 | 70.6 | 74.4 | 74.6 | | 81.5 |
| 5.0 | 71.5 | 73.3 | 77.0 | 70.8 | 88.9 |
| 7.5 | | | | 69.4 | 87.0 |
| 10.0 | 72.3 | | 75.2 | 73.0 | 85.9 |

**Table V**

**Water Absorbed by Cotton Yarn at 93° C. from Solutions of Textile Assistants**

| *Conc. g/l* | *Alkanol B* | *Gardinol WA Double Powder* | *Gardinol CA Powder* | *Product D* | *Soap* |
|---|---|---|---|---|---|
| 0.0 | 67.5% | | | | |
| 0.5 | 69.0 | 64.4% | 70.1% | 62.1% | 64.9% |
| 1.0 | | 68.3 | | | |
| 2.0 | | 68.9 | | | |
| 3.0 | 65.1 | 67.3 | 72.9 | 65.4 | 75.9 |

The indicated lack of efficiency of most penetration agents at elevated temperatures was checked in the following way: Weighed skeins of cotton yarn were wet out at 93°C. by the method of Draves and Clarkson[2]. The skeins were then subjected to the standard centrifugal procedure and it was shown that the average amount of water retained by the skeins was 82% of the weight of the dry cotton. Further tests on this point were made by submerging weighed skeins of unbleached cotton yarn in boiling water for a period of ten minutes. The skeins were removed and subjected to the standard centrifugal procedure. The amount of water retained by the skein was 90% of the weight of the yarn. These data add further proof that the lack of efficiency at elevated temperatures, observed in the solutions of the wetting-out agents is not due to unexpected changes in the nature of the fiber or to a variable expulsion of the liquor at varying temperatures.

The ease of removal of the absorbed solution from yarn is obviously related to the viscosity of the solution. With the exception of soap solutions, the viscosities of the solutions of penetration assistants used in the experimental work reported in this paper are approximately that of water. It was observed from the data reported in Tables III-V that the maximum apparent absorption of water by cotton yarn immersed in soap solutions is uniformly greater at the higher concentrations than the indicated absorption from the solutions of the other assistants. The following tests show that in general this apparent difference is due to a difference in the relative viscosity of the solutions. A stock solution of Gardinol WA Double Powder with gelatin was prepared, such that the solutions of Gardinol WA Double Powder and soap at 25°C. possessed the same relative viscosities at a concentration of 5 grams per liter of the assistant. Tests of the amount of solution retained by the yarn after being run through the standard centrifugal procedure were made over a range of concentrations. Comparisons of the quantity of solution retained by cotton yarn when immersed in solutions of Gardinol WA Double Powder, Gardinol WA Double Powder + gelatin, and soap are made in Table VI.

**Table VI**

**Relationship of Viscosity to Retention of Solution in Penetration Tests**

| *Conc. g/l* | *Gardinol WA Double Powder* | *Gardinol WA Double Powder+gelatin* | *Soap* |
|---|---|---|---|
| 1.0 | 69.1% | 68.5% | 66.4% |
| 2.0 | 81.2 | 84.1 | 79.5 |
| 3.0 | 83.6 | 88.5 | 85.2 |
| 5.0 | 81.5 | 87.5 | 94.1 |

The data in Table VI show that solutions prepared from the same assistant but with different viscosities at comparable concentrations differ appreciably from each other in the values which they give for retention of the solution.

(Continued on page 717)

# Rayon Dyeing and Finishing-17

*By* **B. L. HATHORNE**
*Consulting Textile Chemist*

## CHAPTER IX—DYEING AND FINISHING OF RAYON AND RAYON CONTAINING FLAT WOVEN GOODS

(*Continued from page 654, November 6th issue*)

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THIS subject is so broad that a complete detailed description of all apparatus and procedures would destroy the purpose of this chapter, which is to present the dyeing and finishing of rayon in a clear, concise manner.

Only the better known apparatus and procedures for handling flat woven rayon and rayon-containing fabrics will be described in this chapter. As a matter of fact, it would be unfair on the part of the writer to discuss special procedures and methods of finishing various specialty fabrics with which his work has necessarily brought him into contact. The writer has consistently refrained from disclosing any of the trade secrets that have been at one time or another purposely, or inadvertently, disclosed to him.

### DISCUSSION OF GREIGE GOODS

We have attempted to divide the discussion of rayon and rayon-containing flat woven greige goods into a few broad divisions from the viewpoint of similarity of impurities (or materials other than fiber substance), faults present in greige goods and the similarity in methods of handling in the dye house; rather than from the viewpoint of fabric construction and nomenclature. Only the commercially important (from yardage viewpoint) fabric divisions have been discussed. Specialties and group variations have been purposely omitted.

#### Flat Crepes

The term rayon flat crepe usually designates a fabric consisting of an untwisted (except for the usual 2½ turns put in by the rayon manufacturer) rayon warp combined with a relatively highly twisted filling yarn. The fabric is so designed that the twisted filling slowly shrinks during the scouring operation, thus producing the well known crepe effect. Properly designed and finished flat crepes present a very pleasing appearance and are soft and pliable with respect to hand. These fabrics will stand a surprising amount of wear and washing without objectionable deterioration of any sort.

Many fabrics sold as rayon flat crepes do not coincide with the definition of a rayon flat crepe as given above. Regardless of terminology, these fabrics are usually handled as flat crepes and, in general, contain the same impurities when in the greige state.

So many factors enter into the production of flat crepe fabrics that close cooperation between the fabric manufacturer and the finisher is absolutely necessary in order to produce the best possible flat crepe at a given cost. Unfortunately, the effect of some of the factors influencing the final appearance of flat crepe fabrics is often overlooked by converters responsible for the design of the same.

Minor changes in fabric design, for instance the inclusion of as few as 2 or 3 ends per inch, sometimes make the difference between a sleazy fabric showing warp breaks and a firm fabric relatively free from "open warp" faults.

Improper filling design—particularly lack of coordination between the number of picks per inch and the turns of twist employed—is responsible for the production of many inferior flat crepe fabrics. In an endeavor to produce cheaper fabrics, the filling picks have been continuously reduced until the danger point has been reached and passed. As a result, many inferior flat crepe fabrics have appeared on the market.

To the dyer and finisher the necessity of reducing twist as picks per inch are reduced, and also the necessity of changing the nature of the sizing material used in the filling in correlation with reduction of filling picks, is at once readily apparent. Judging from fabrics submitted to the finisher for processing, fabric designers do not properly appreciate the relationship existing between the pick count, twist, filling, sizing, and the dyeing and finishing operations.

Flat crepe fabrics generally contain both left and right twist yarns in the filling. The usual construction is: 2 picks of left twist yarn followed by 2 picks of right twist. Twist counts employed in general vary from forty to sixty turns per inch.

Variations in the twist count of the filling yarns produce very serious variations in the appearance of the finished product. Special methods of handling often overcome, in part or entirely, the trouble due to use of filling yarns the twist count of which varies.

The use of an improper sizing material in the filling can result in the production of decidedly inferior fabrics, even though all possible precautions be observed during the scouring and dyeing operations.

Whereas rayon flat crepe fabrics contain the usual impurities of grease, dirt, etc., encountered in all woven fabrics; the extreme scouring procedures necessary to produce the desired results in a flat crepe fabric so successfully remove these various impurities that it is not necessary to discuss them further.

The constant effort of fabric manufacturers to produce a fabric almost as good as that of competitors, and selling at a price just under competitors, has resulted in a continual lowering of quality. This vicious practice has finally defeated its own ends, as it has resulted in the production and sale of large quantities of inferior flat crepe fabrics, which in turn has caused these fabrics to lose their popularity with the public. It is to be presumed that flat crepes will not regain their popularity until quality fabrics are again produced.

### Imitation Flat Crepes

This heading covers the vast group of fabrics designed to imitate flat crepe fabrics in appearance at a cheaper cost. There are so many variations in these imitation flat crepes that a complete listing would involve unnecessary detail. It is sufficient to say that these fabrics contain the same impurities as do ordinary flat crepes, and are in general handled in the same manner.

One successful imitation flat crepe has been produced by weaving a twisted cotton warp (2 threads alternating left and right twist) with an untwisted rayon filling. This fabric possesses the general appearance of a flat crepe fabric, particularly at a distance of 3 or 4 feet, for example, when observed in a store window.

In a way it is unfair to regard such a fabric as an imitation, as this particular fabric gives the consumer every excellent service. In characteristics it varies from a true flat crepe only with respect to feel and draping qualities.

### Taffetas, Twills, Lining Cloths, and Related Fabrics

Under this heading we will consider all flat woven rayon and rayon-containing fabrics, excluding acetate combinations, in which the warp and filling yarns are given no additional twist by the fabric manufacturer. Obviously, this group must include such fabrics as alpacas, corset cloths, rayon-containing shirting fabrics, bed spreads, etc.

From a dyeing and finishing viewpoint, the above listed fabrics must be handled in a very similar manner.

These fabrics usually contain warp sizing materials that must be removed simultaneously with, or prior to, the dyeing operation, as well as the usual mechanical impurities acquired during fabric manufacture.

In addition, many of them contain cotton yarns, which must of course be thoroughly cleansed and penetrated during dyeing and finishing. As a matter of fact, the dyeing and finishing procedure for cotton containing rayon fabricss are, from a scouring angle, usually designed to accommodate the cotton, as treatments that will successfully cleanse cotton must also clean rayon. If rayon alone was present the treatment could even be much more mild and economical.

### Voiles and Georgettes

Under this heading we will consider all fine denier flat woven fabrics manufactured from highly twisted yarns. As in the case of flat crepe fabrics, the scouring treatments necessary to produce a proper appearance are sufficient to successfully remove all impurities present in voiles and georgettes. As a matter of fact, the sizing materials used in the production of voiles and georgette yarns are usually very easy to remove, as they generally consist of oils applied from an emulsion bath.

Voile and georgette greige fabrics are apt to contain two fabrics *flaws* that, when observed in the finished fabric, are usually blamed upon the dyer and finisher during fabric manufacture. These flaws are:

1. Twist variations.
2. Tight warp threads.

The fact that twist variations must produce a variation in the appearance of the finished fabric is at once obvious. The fact that twist variations may result in the production of a torn fabric and may increase the dyeing and finishing costs is not so readily apparent.

Uneven filling twists allow uneven shrinkage to take place during the scouring operation, thus causing the dyed fabric to go to the tenter frame with variations in width from end to end of the piece. Under normal tentering conditions the widest section of the fabric will pass from the tenter frame satisfactorily, whereas the narrow bands caused by the presence of high twist will tear at the selvedge, thus producing second-quality merchandise.

Extremely tight warp threads can be detected in the greige fabric. Minor variations in tension cannot be detected until the fabric has been scoured. It is very important that tight warp threads be identified, and made known to the fabric manufacturer, as they cause pronounced warp streaks which are often mistaken for dye variations, and which indeed, will take the dye differently unless special dyeing precautions are observed.

### Satins

Under this heading we will consider both the plain and crepe back satin fabrics. No other fabric is as completely dependent on fabric design for the production of satisfactory result as is a satin fabric. It is essential that fabric design and construction shall be correct in all details.

Some designers, in an attempt to produce extremely economical lustrous satins, float the warp yarns over so many picks in sleazy constructions that it is difficult to properly handle the fabrics in finishing plants without destroying or injuring the face. Such fabrics cannot give the consumer full satisfaction, except when used as decorative fabrics and for purposes that do not entail wear and possible abrasion.

(Continued on page 709)

PROCEEDINGS OF THE
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NOVEMBER 20, 1933

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## The Determination of

# Organically Combined Sulfuric Anhydride

## in Sulfonated Oils

*By* RALPH HART
*Chairman, Sub-Committee on Sulfonated Oils—Report No. 2*

IN THE first report[10] the sub-committee on the Analysis and Grading of Sulfonated Oils recommended a method of test for water in sulfonated oils. In the second or present report various methods for determining organically combined sulfuric anhydride are discussed and two proposed methods are outlined. There has been no change in the personnel of the sub-committee since its formation, which consists of the following members:

Ralph Hart, 1440 Broadway, N. Y. C., Chairman.

J. Andrew Clark, Dutchess Bleachery, Inc., Wappingers Falls, N. Y.

Geo. P. Feindel, Union Bleachery, Greenville, S. C.

Stephen K. Ford, Marden-Wild Co., Somerville, Mass.

Arthur L. Fowler, Jr., American Cyanamid & Chemical Corp., Woodbridge, N. J.

A. H. Grimshaw, N. C. State College, Raleigh, N. C.

C. P. Gulick, National Oil Products Co., Harrison, N. J.

R. A. Pingree, U. S. Finishing Co., Providence, R. I.

I. Silverman, L. Sonneborn Sons, Inc., Belleville, N. J.

W. S. Williams, Mt. Hope Finishing Co., North Dighton, Mass.

Mention should also be made of the following men who have helped with the analytical work at the various laboratories:

G. L. Dozier, Union Bleachery.

M. B. Hart, The Hart Products Corp.

A. C. Hayes, North Carolina State College.

S. Kaswell, L. Sonneborn Sons, Inc.

Miss E. Klein, L. Sonneborn Sons, Inc.

E. Segessemann, National Oil Products Co.
Fred R. Tripp, Mt. Hope Finishing Co.

A reliable and expedient method for the determination of organically combined $SO_3$ in sulfonated oils is granted to be of considerable importance to the trade. This is principally due to the fact that the colloidal properties of the finished product, such as solubility in water, miscibility with oils, emulsive capacity, stability towards hard water, salts and acids, surface-tension-lowering and wetting-out properties, etc., depend primarily upon this ingredient. There are a number of methods available for making this test, and a description of the more important ones follows:

### Barium Sulfate or Herbig Method

The Herbig method[12], the first to be used in commercial laboratories, consists in decomposing or hydrolyzing the sulfonated oil by boiling with hydrochloric acid and determining the total sulfur in the water layer as barium sulfate. The inorganic sulfate originally present in the oil is then determined in another sample, also as barium sulfate, by dissolving the oil in a solvent and washing it free from sulfate with a concentrated solution of sodium chloride. The combined $SO_3$ evidently is the difference between the two determinations. This method obviously can be used only for oils that are decomposed by acids, (i.e., the ester type) and which do not emulsify in the presence of solvents and sodium chloride solution. The Herbig method has now been displaced to a great extent by the more rapid and convenient sulfuric acid-titration method[3], described later, but as it is still the official method of the Wissenschaftliche Zentralstelle für Oel- und Fettforschung (Wizöff)[18], it is thought advisable to give below the procedure in detail:

(a) Decomposition of the Oil—If the fatty acid content of the oil under test is approximately known, 8 g. in the case of 50 per cent oils, or 4 g. in the case of 100 per cent oils, is weighed out for analysis. If fatty acid content is not known, 6-8 g. is dissolved in 25 c.c. of distilled water, 50 c.c. of conc. HCl (sp. gr. 1.19) added, and the mixture heated in an extraction flask with reflux condenser until the fat has entirely separated, in any case for an hour at least. After cooling, it is transferred, together with a little distilled water and ether, into a separating funnel; and when the two layers have separated, the clear acid water is removed and shaken up twice with 25 c.c. of ether. The two ether solutions are washed free from acid by repeated shaking up with 20 c.c. water. If emulsions form or fatty particles separate out again when the wash water is acidulated with HCl, the product under test still contains some sulfo acids, and cannot be tested under the scheme being described.

(b) Determination of Total Sulfuric Acid—The combined acid and wash waters from the fatty acid determination are neutralized with ammonia (methyl orange indicator), then again acidified by addition of 1 c.c. of conc. HCl, made up to about 400 c.c. total volume, and the sulfuric acid estimated by precipitating at the boil with barium chloride solution in the usual way. (c) Determination of Inorganically Combined Sulfuric Acid—5 to 7 g. of oil is shaken up in a separating funnel with 10 c.c. saturated sulfate-free common salt solution, 10 c.c. ether, and 15 c.c. amyl alcohol, the clear salt solution separated from the ether, and then washed three times with 10-20 c.c. of conc. salt solution. The combined salt solutions are made up to 250 c.c., 1 c.c. of concentrated HCl is added, and the sulfuric acid precipitated, as already indicated. (d) Determination of Organically Combined Sulfuric Acid—This is not directly estimated, but calculated as the difference between total and inorganically combined sulfuric acid.

### Combustion Methods

According to the combustion method[6], the sample is either fused with potassium nitrate and sodium carbonate in a crucible, or ignited in a bomb in the presence of potassium perchlorate and sodium peroxide. In either case the total $SO_3$ is determined as barium sulfate in the water extract. As in the Herbig method, the inorganic sulfate in the oil must be determined separately. Evidently the combustion methods may be used also to determine sulfur in oils that are not hydrolyzed by acids.

### Ash-Titration Method

This direct method[9], as well as the two following, was originally suggested by the chairman. It is based upon the fact that when a sulfonated oil is ashed in presence of excess alkali, all of the organically combined $SO_3$ is converted into sodium sulfate, thus: $2\ R\text{-}O\text{-}SO_3\ Na + 2\ NaOH \rightarrow 2\ Na_2SO_4 + H_2O +$ etc. It is evident that for every molecule of organically combined $SO_3$ one molecule of caustic soda is neutralized. Hence by determining the loss in titrable alkali after ignition, it is possible to calculate the organically combined $SO_3$ directly; i.e., without finding the inorganic sulfate in the original oil. Excess alkali seems to affect the porcelain crucible in which the sample is ignited, causing high results. As other methods are available free from this objection, the ash-titration method was not further investigated.

### Sulfuric Acid-Titration Method

The sulfuric acid-titration method first appeared in the literature in 1917[8] and since then has been adopted by several technical organizations[1, 7, 18], either as their official or alternative method of test for combined $SO_3$ in sulfonated oils. It depends upon the fact that when a sulfonated oil of the ester type is boiled with excess sulfuric acid hydrolysis or decomposition take place, producing an increase in the mineral acidity of the mixture that corresponds quantitatively to the amount of organically combined $SO_3$ liberated. Under the proper conditions the hydrolysis is complete, and the subsequent change in acidity may be determined accurately. The change that takes

place upon boiling with acid is represented by the following equation:

$$R\begin{matrix}/OSO_3Na\\ \backslash COOH\end{matrix} + H_2O = R\begin{matrix}/OH\\ \backslash COOH\end{matrix} + NaHSO_4$$

That is, for every molecule of combined sulfuric anhydride there is liberated one hydrogen equivalent of mineral acid, in the form of $NaHSO_4$. In the presence of soap some of the acid is lost by neutralization as follows:

$$2R\begin{matrix}/COONa\\ \backslash OSO_3Na\end{matrix} + H_2SO_4 = 2R\begin{matrix}/COOH\\ \backslash OSO_3Na\end{matrix} + Na_2SO_4$$

Hence to find the total increase in acidity after the boiling, two determinations are necessary; namely, (1) the decrease in acidity due to the neutralization of the acid by the soap, given by the alkalinity of the sample and designated as "A"; and (2) the increase in acidity after boiling the sample with sulfuric acid, designated as "F". Both determinations are made volumetrically in presence of methyl orange indicator. In the case of sulfonated oils high in alkalinity or low in organically combined $SO_3$, or both, there may actually be a decrease in acidity after boiling with the acid, in which case "F" would be negative. The formula for calculating the organically combined $SO_3$ is as follows:

Percent Combined $SO_3$ =

$$\frac{SO_3\ (A + F)}{10} = \frac{80\ (A + F)}{10} = 8\ (A + F)$$

Where "A" represents the alkalinity of the sample and "F" (which may be positive or negative), the increase in acidity after boiling, in both cases expressed as milliliters of N/1 solutions per gram of sample.

The sulfuric acid-titration method is rapid, requires a minimum of attention and manipulation, and the results are reliable. All members of the committee were familiar with the method and in favor of investigating it in preference to the other methods. Adverse criticisms of the method deal mainly with the following three points: (a) incomplete decomposition of the sulfate group, (b) difficulty of titrating in the presence of fatty matter and (c) unreliable end-points obtained in the presence of certain titrable salts, such as sodium acetate.

Professor K. Nishizawa[13] in an exhaustive series of experiments has shown that sulfonated oils of the ester type are completely hydrolyzed or decomposed by normal sulfuric acid at boiling temperatures in 40-50 minutes. This committee has investigated the difficulty in obtaining correct end-points in the presence of fat, and finds that with the aid of salt and ether very accurate titrations are readily obtained. It is to be admitted, however, that the presence of sodium acetate or other titrable salts of that type in the sulfonated oil interferes with the end-points and renders the method unreliable. In such cases a new method, called the ash-gravimetric method (described later) and hitherto not published, was found to yield accurate and concordant results.

### Ash-Gravimetric Method

This new direct method[11] was suggestd by the chairman as an alternative procedure and also to supplant the sulfuric acid-titration method in certain samples where the latter cannot be used; e.g., in the presence of sodium acetate. According to this method, the sulfonated oil is dissolved in ether or other solvent, sufficient mineral acid added to decompose the soap, and the ether solution washed with saturated salt solution. Traces of salt are removed by chilling and filtering, the ether in the filtered solution is then evaporated and the residue ashed. The ash represents one-half of the combined $SO_3$ in the form of sodium sulfate, in accordance with the following reaction: $2ROSO_3\ Na = Na_2SO_4 + SO_3 +$ etc.

Laboratory tests indicate that the new method will determine the combined $SO_3$ not only in the usual sulfonated (sulfated) oils but also in oils of the true sulfonic type; i.e., sulfonated oils that are not decomposed upon boiling with mineral acids, including sulfonated mineral oil. In fact, the method seems to be applicable to all types of sulfonated oils, provided they may be completely extracted from salt solution without causing troublesome emulsions.

According to K. Nishizawa and K. Winokuti[14], sulfonated oil is least soluble as its mono-sodium compound (i.e., free from soap); and in that form it is entirely insoluble in, or may be completely extracted from, saturated solutions of either sodium chloride or sodium sulfate. Hence in the procedure given at the end of this report, enough acid is added to the sample before extracting just to decompose the soap. A very slight excess of acid is permissible. Sodium chloride, rather than sodium sulfate, is used for the first washes because it gives a much sharper color change with methyl orange upon acidifying and there is no tendency for the salt to crystallize. The purpose of the final wash with saturated sodium sulfate solution is to dehydrate the ether extract as much as possible. This is accomplished by cooling and crystallizing the last traces of salt solution remaining in the ether extract.

The special procedure in the presence of ammonia is required only where the combined $SO_3H$ group is partly or wholly neutralized by that alkali. Unless converted into the sodium salt, the combined $SO_3$ would be too low, due to loss of ammonium salt upon ignition. Ammonium soaps, however, do not interfere with the regular method.

When the sample is acidified in the presence of sodium acetate, as outlined, the acetate is probably only partly decomposed; the water layer, as well as the ether extract, may contain both free acetic acid and sodium acetate. This, however, does not interfere with the method, since during ignition the acetic acid is entirely volatilized, and the undecomposed sodium acetate is removed by the

final sodium sulfate wash, followed by chilling and filtering.

### Results by the Ash-Gravimetric Method

The reliability of the ash-gravimetric method, and the extent of its application, may be noted in examining Table I, in which is given the combined $SO_3$ contained in a number of oils, determined by the ash-gravimetric method and, where possible, also by the acid-titration method. This work was done at the chairman's laboratory. Attention is called to the following analyses in the Table. The two methods gave check results with Sample No. 1, which represented a concentrated sulfonated (sulfated) castor oil of the usual type. In the case of Sample No. 2, which consisted of a mixture of equal parts of the previous sample and a solution of sodium acetate, the old method fell down completely on account of the difficulty in obtaining correct end-points. No particular difficulty, however, was experienced in analyzing it by the new ash-gravimetric method, which gave a result almost identical with the calculated value; namely, 2.58% as compared with 2.61% by calculation. The old method gave zero results for the combined $SO_3$ in all true sulfonic acid products, such as Samples No. 4, 6, 7, 8 and 9, representing a true sulfonic acid oil, a sulfonated ester, a sulfonated aromatic hydrocarbon and two samples of sulfonated mineral oils, respectively. The combined $SO_3$ by the new method, on the other hand, varied from 3.0% in Sample No. 4 to 14.2% in Sample No. 8. Further details about this method are given elsewhere[11].

**Table I**

**Organically Combined Sulfuric Anhydride in Sulfonated Compounds by the Acid-Titration and Ash-Gravimetric Methods**

| Sample No. | Description | —Combined $SO_3$, Per Cent— Acid-Titration (Old) Method | Ash-Gravimetric (New) Method |
|---|---|---|---|
| 1. | Sulfated castor oil..... | 5.19 | 5.23 |
| 2. | Sulfated castor oil (a)..... | ? | 2.58 (g) |
| 3. | Sulfated olive oil (b)..... | 3.82 | 3.90 |
| 4. | Sulfonated oil (c) ..... | 0.00 | 3.00 |
| 5. | Sulfonated fatty alcohol..... | 15.80 | 16.18 |
| 6. | Sulfonated fatty ester (d)..... | 0.00 | 6.25 |
| 7. | Sulfonated aromatic hydro-carbon (e) ..... | 0.00 | 10.70 |
| 8. | Sulfonated mineral oil..... | 0.00 | 14.21 |
| 9. | Sulfonated mineral oil (f)..... | 0.00 | 4.88 (h) |

(a) Equal parts of Sample No. 1 and 5% solution of anhydrous sodium acetate.
(b) Neutralized with ammonia.
(c) Saponifiable, true sulfonic acid type.
(d) Fatty acid combined with sulfo alkylamine.
(e) Isobutyl naphthalene sodium sulfonate.
(f) One part of Sample No. 8 and two parts of 25% sodium sulfate solution.
(g) Calculated — 2.61%.
(h) Calculate — 4.74%.

### Experimental

Committee Sample B, representing a sulfonated castor oil, with about 25% of water, was submitted to the members of the committee with instructions to determine the combined $SO_3$ by the acid-decomposition method and by the ash-gravimetric method. After considerable experimenting, the procedures given at the end of this report were finally developed and approved by the committee. The analyses of the oil were repeated, using the new procedures. The results are given in Table II. It will be noticed that the greatest difference and the average deviation by the acid-titration method were 0.29% and 0.06%, respectively; and by the ash-gravimetric method, 0.35% and 0.09%, respectively. It is particularly to be noted that the mean results by the old and new methods were 5.22% and 5.20%, respectively, or a difference of only 0.02%.

**Table II**

**Results of Combined Sulfuric Anhydride in a Sample of Sulfonated Castor Oil (Sample B) by the Acid-Titration Method; Also by the Ash-Gravimetric Method**

| | Combined $SO_3$, Per Cent Acid-Titration Method | | | | Combined $SO_3$, Per Cent Ash-Gravimetric Method | | | |
|---|---|---|---|---|---|---|---|---|
| Analyst | I | II | Ave. | Deviation from Mean | I | II | Ave. | Deviation from Mean |
| Clark | 5.23 | 5.24 | 5.24 | 0.02 | 5.37 | 5.37 | .537 | 0.17 |
| Feindel | 5.36 | 5.42 | 5.39 | 0.17 | ... | ... | ... | ... |
| Ford | 5.15 | 5.20 | 5.18 | 0.04 | 5.05 | 4.98 | 5.02 | 0.18 |
| Grimshaw | 5.23 | 5.28 | 5.26 | 0.04 | ... | ... | ... | ... |
| Gulick | 5.07 | 5.12 | 5.10 | 0.12 | 5.04 | 5.10 | 5.07 | 0.13 |
| Hart | 5.18 | 5.14 | 5.16 | 0.06 | 5.26 | 5.18 | 5.22 | 0.02 |
| Pingree | 5.16 | 5.18 | 5.17 | 0.05 | 5.22 | 5.17 | 5.20 | 0.00 |
| Silverman | 5.30 | 5.19 | 5.25 | 0.03 | 5.20 | 5.24 | 5.22 | 0.02 |
| Williams | 5.19 | | 5.19 | 0.03 | 5.27 | 5.29 | 5.28 | 0.08 |
| Mean | | | 5.22 | | | | 5.20 | |
| Greatest difference | | | 0.29 | | | | 0.35 | |
| Average deviation | | | 0.06 | | | | 0.09 | |

The oil mentioned previously was mixed exactly with an equal part of a 5.0% solution of anhydrous sodium acetate, Sample B-1, and submitted to the committee for analysis of the combined $SO_3$ by the two methods. After some experimenting, the committee unanimously agreed that the acid-decomposition method, due to uncertainty in determining the correct end-points, gave unreliable results, and that it was consequently inapplicable in the presence of sodium acetate or similar titratable salts. Fortunately the ash-gravimetric method gave results,

**Table III**

**Results of Combined Sulfuric Anhydride in Sample of Sulfonated Castor Oil (Sample B-1), Containing 2.5% Anhydrous Sodium Acetate, by the Ash-Gravimetric Method**

| | —Combined $SO_3$, Per Cent— | | | |
|---|---|---|---|---|
| Analyst | I | II | Ave. | Deviation from Mean |
| Clark | 2.51 | 2.58 | 2.55 | 0.01 |
| Ford | 2.48 | 2.52 | 2.50 | 0.06 |
| Fowler | 2.52 | 2.50 | 2.51 | 0.05 |
| Grimshaw | 2.51 | 2.57 | 2.54 | 0.02 |
| Gulick | 2.65 | 2.54 | 2.60 | 0.04 |
| Hart | 2.63 | 2.64 | 2.64 | 0.08 |
| Pingree | 2.67 | 2.61 | 2.64 | 0.08 |
| Silverman | 2.50 | 2.54 | 2.52 | 0.04 |
| Williams | 2.46 | 2.57 | 2.51 | 0.05 |
| Mean | | | 2.56 | |
| Calculated | | | 2.60 | |
| Greatest difference | | | 0.14 | |
| Average deviation | | | 0.05 | |

shown in Table III, which proved highly satisfactory. It will be noticed that the greatest difference and the average deviation were only 0.14% and 0.05%, respectively; furthermore that the mean varied from the calculated value by only 0.04%.

### Comments and Suggestions

The following comments and suggestions were received from members of the committee:

J. Andrew Clark: The end-point in the acid-titration method would be much sharper if only two or three drops of methyl orange indicator solution were used instead of the 5 c.c. as directed. In committee sample B-1, containing sodium acetate, I found the greatest difficulty in determining the end-point. In the ash-gravimetric method we used a 65 c.c. tall silica crucible, and after evaporating off the solvent, we placed a small wick in the oil and lighted it. This gave a convenient method of evaporating the oil without much carbon formation and permitted easy ashing. We found no particular difficulty in running this method.

S. K. Ford: The methyl orange indicator does not seem to be retained by the ether as has been claimed. In the analysis of Sample B-1, the end-points were very bad and entirely unsatisfactory with the acid-titration method. I did not have any difficulty, however, with the ash-gravimetric method except for the creep of the ether solution. If it yields accurate results, the method is not difficult.

George P. Feindel: In the acid-titration method we experienced great difficulty from bumping while refluxing, and found that beads did not eliminate the trouble. It was found, however, that a small glass rod—bent in the shape of a hairpin and placed in the flask with one end in the liquid and resting on the bottom, and the other end reposing on the side of the flask—gave a much more even reflux. It is our opinion that with a few minor modifications, and provided there are no interfering substances present, the acid-titration method should prove to be a very satisfactory standard.

Arthur L. Fowler: In the acid-titration method I do not standardize the acid solution very accurately, but run a blank with as many determinations as need to be run. The blank is run first (i.e., the titration) and the samples matched to the end-point of the blank. With this procedure there is little chance of any error entering because of faulty end-points, and the normality of the solution is obtained correctly since the solution has been subjected to the same conditions as the sample. I "picked up" this method from Dr. Bumcke. From my experience the ether does not extract the indicator in the titrations. In analyzing Committee Sample B-1 by the acid-titration method it was found difficult to obtain very close check determinations when calculating the alkalinity (A).

The ash-gravimetric method presented no difficulties; but in spite of the fact it was carefully performed, very close agreement on checks were not obtained, although the average of two determinations agrees with the average result obtained by the acid-titration method. A little more experience with the method is needed.

A. H. Grimshaw: In analyzing Sample B-1 by the acid-titration method we experienced considerable difficulty in getting end-points after the sulfuric acid digestion, etc. We added more than the given amounts of ether and salt, but were unable to obtain a definite end-point. Therefore the results obtained are far from being consistent. Sodium acetate interferes with this method, as it apparently hydrolyzes to form free alkali.

In the ash-gravimetric method there was some trouble due to creeping. This was checked somewhat by substituting a size No. 2 crucible. The latter was half filled with the ether extract and the ether allowed to evaporate slowly over warm water. By passing a stream of warm air into the crucible and over the surface of the liquid, evaporation was accelerated and the rim of oil prevented from rising to the top of the crucible.

We suggest the adoption of the ash-gravimetric method only in case sodium acetate is known to be present. Otherwise it would seem better to use the titration method since it is quicker. Very good check results were obtained with the ash-gravimetric method.

C. P. Gulick: The acid-titration method seems to be the most convenient and the least time-consuming of the methods suggested. We found that in analyzing Sample B-1 by the acid-titration method the end-point on titrating was very uncertain; and for this reason we would not attach too great importance to the results obtained by this procedure. Concerning the calculations, we wonder if it would not be advisable to change them to a Na-1 per cent basis.

We found the ash-gravimetric method very satisfactory in every respect. We believe it to be theoretically sound and are convinced by our laboratory experience that any analyst possessing a fair degree of skill will be able to obtain satisfactory results by this procedure. We would not hesitate to recommend this method as an alternative in cases where the application of the acid-titration method is of doubtful value.

Ralph Hart: At first we were unable to get check results (which were also abnormally low) on Sample B by the acid-titration method. Many changes in the procedure were tried in order to locate the cause for the discrepancies. Ground-glass connection were substituted for cork stoppers; longer boiling, continuous agitation, smaller samples, and more acid were also tried; but with no improvement. In fact, where all precautions were applied, the results were even lower and in some cases actually zero! The difficulty was finally traced to the glass beads, which were old and partly

crystallized and devitrified. They had been used to prevent bumping in the determination of water by the proposed A.A.T.C.C. method. These beads were thoroughly boiled out before use; nevertheless a blank test showed that they were absorbing acid. In view of this experience we suggest that new beads of resistance glass be used for each determination and that a blank test be run at the same time with the sample. In that case it would not be necessary to standardize the sulfuric acid used in decomposing the sample. Perforated beads were found to be more effective than solid beads in preventing bumping. Pumice stone is excellent in this respect, but it absorbs acid, which it gives up very slowly when the solution is titrated.

The end-point in presence of sodium chloride and ether is remarkably sharp and sensitive. On the other hand, in a saturated solution of sodium sulfate the end-point is rather uncertain, changing from brown to pink. The conventional procedure specifies 25 c.c. of N/1 sulfuric acid. It is conceivable that with samples of high alkalinity there may not be enough excess acid to effect complete decomposition of the oil. Therefore it is suggested that there be added 25 c.c. normal acid in excess of the amount required to neutralize the alkali in the sample.

R. A. Pingree: Contrary to Nishizawa's statement, I find that methyl orange is not extracted from the aqueous solution by the ether. In fact, I find this indicator to be practically insoluble in ether. I was able to obtain very sharp end-points (1 drop of N/2 acid) by using 5 drops of methyl orange indicator (0.1% solution) and titrating in the presence of the ether-oil layer. When 5 ml. of methyl orange is used, the solution is colored to such an extent that the end-point is obscured. In fact, Kolthoff (volumetric analysis Kolthoff and Furman) states that for every 25 c.c. of solution one drop of 0.1% methyl orange solution should be used. In decomposing the sample with sulfuric acid we clamped the flask and condenser above a chrome gauze and adjusted the flame so that the acid boils at such a rate that vapors do not rise in the condenser tube higher than 6" from the top. In this way there is no evaporation loss and little attention is required. We have made trials with the glass beads sent us by the chairman and find that they absorbed large amounts of acid. It is evidently of prime importance that the beads used should be of chemically resistant glass or that a blank test be run with the beads beforehand. We find when using a 10-gram sample of oil, 25 ml. of N sulfuric acid in excess of that required to neutralize the total alkali is sufficient for complete decomposition. With the above ratio of oil and acid, one hour at the boil under a reflux condenser is more than time enough for complete decomposition. The agitation caused by boiling is sufficient to allow the decomposition to reach completion.

In the following analyses, normal acid and alkali were used throughout. For organic $SO_3$, 25 ml. of acid was used in excess of that required to neutralize the total alkali. To determine whether one hour of boiling was sufficient to completely decompose the oil, sample 3F was boiled only one-half hour. This result indicates that one hour is more than ample time for decomposition:

| *Sample* | *Weight gms.* | $H_2SO_4$ *Ml.* | *Time of boiling, Hrs.* | *NaOH Ml.* | *A* | *F* | $SO_3$ *%* |
|---|---|---|---|---|---|---|---|
| 1 A | 9.1785 | 4.70 | .. | .. | 29.16 | .. | 5.11 |
| 1 F | 8.4581 | 30.00 | 1 | 30.25 | .. | 6.70 | . |
| 2 A | 11.2134 | 5.80 | .. | .. | 29.37 | .. | 5.20 |
| 2 F | 9.1709 | 32.00 | 1 | 32.35 | .. | 7.10 | .. |
| 3 A | 12.4110 | 6.40 | .. | .. | 29.29 | .. | 5.15 |
| 3 F | 10.4381 | 30.00 | ½ | 30.50 | .. | 6.82 | .. |

I suggest use of exactly the same amount of acid in the blank as that use in the sample. In this way it is only necessary to subtract one titration from the other. I also suggest a more simplified procedure for calculating results, as follows:

1. Alkalinity: Express as ml. of N/1 $H_2SO_4$ required to combine with 1 gram of oil. Let this figure equal A.
2. Acid-Decomposition: Express both $H_2SO_4$ and NaOH used in terms of ml. of N solution per gram of oil. Let ml. $H_2SO_4$ equal B and ml. NaOH equal C.
3. Calculation of Organic $SO_3$:
   $B - A = X =$ ml. of free $H_2SO_4$ for decomposition.
   Then obviously—
   $C - X = Y =$ ml. of N/1 $H_2SO_4$ formed in decomposition from organic $SO_3$.
   To convert to per cent $SO_3$:
   $Y \times 8.00 = \%\ SO_3$.

In the analysis of Sample B-1 the end-points due to the buffering action of the sodium acetate were very poor and difficult to judge. The ash-gravimetric method is quite long and time-consuming but seems to produce consistent results. Considerable analytical technique is required to prevent loss during manipulation. I also find that salt-free ether layer after cooling and filtering twice will deposit a further precipitate if allowed to stand overnight at room temperature. My opinion on the procedures is that the acid-titration method should be adopted as a standard method, with the ash-gravimetric as an alternative to be used only in the presence of acetates (or other water soluble organic acids) as shown by qualitative test.

I. Silverman: We agree that the sulfuric acid method can give erroneous results if the beads used have already gotten to a condition where they may influence the test. We, of course, get around this by not using

any set of beads too many times. Inspection of the beads before using gives an indication as to whether they can be used. However, we believe the idea of running a blank in order to take care of the effect of the beads should obviate differences due to the beads.

Our laboratory could get no results at all with Sample B-1 by the acid-titration method. We believe the method to be absolutely worthless where sodium acetate is present, as in this sample.

The ash-gravimetric method seems to work quite well, once the operator becomes accustomed to the method. While we believe the method to be rather complicated as compared with the acid-titration method, we still believe that with a little practice it will make a good method for determining combined sulfate where acetates have been found present by a qualitative test.

Walter S. Williams: The acid-titration method proved very satisfactory even though two separate samples had to be weighed out at the start. The two titrations are easy to make.

### Summary and Recommendations

In this investigation, the committee took it for granted that the method for organically combined $SO_3$ in sulfonated (sulfated) oils by decomposition with sulfuric acid, followed by titration, was fundamentally sound. This has been proved by the investigations of Bauer[2, 3, 4], Bumcke[5], Hart[8], Nishizawa[13], Riess[15] and by committees of the American Leather Chemists Association[16, 17]. Hence, the work of this committee consisted essentially in investigating certain criticisms of the method and in improving its accuracy. The committee finds that there is little tendency for the ether to extract the methyl orange indicator from the water layer, at least not enough to interfere with the titrations, and that in the presence of sodium chloride and ether the end-points are remarkably sharp. It recommends the following changes in the usual procedure: A blank determination of the decomposition step, fresh beads of chemically resistant glass and preferably perforated, ground-glass connection, five drops of a 0.1% methyl orange solution for the titrations, and an amount of sulfuric acid for the decomposition to give the same excess of acid in all samples. The results obtained by the committee on a sample of sulfonated castor oil by the final procedure were gratifying; the mean value of combined $SO_3$ was 5.22%, the greatest difference 0.29%, and the average deviation 0.06%.

The committee also finds the acid-titration method yields unreliable results in the presence of sodium acetate or similar titratable salts on accounts of poor end-points. Evidently it is also not applicable to sulfonated products which are not hydrolyzed upon heating with mineral acids, i.e., true sulfonic acid types. Fortunately the ash-gravimetric method was developed, a new method hitherto not published, which can be used in both cases and may also serve as a check method for the other procedure. The committee analyzed a sample of sulfonated castor oil containing the maximum amount of sodium acetate that it could absorb without separating (about 2½% of the anhydrous salt) and obtained the following results for the combined $SO_3$: mean 2.56 %, as compared with 2.60% by calculation, greatest difference 0.14%, and an average deviation of 0.05%.

In view of these findings, the committee believes that the following two procedures are the most suitable for official methods: (a) the sulfuric acid-titration method, and (b) the ash-gravimetric method.

### Proposed Standard Method of Test for Organically Combined Sulfuric Anhydride in Sulfonated (Sulfated) Oils

### A.A.T.C.C. Sulfuric Acid Titration Method

*Scope*:

1. This method of test determines the organically combined sulfuric anhydride existing in a sample of sulfonated (sulfated) oil by boiling the sample with sulfuric acid and titrating the products of reaction. This method applies only to sulfonated oils that split off their combined $SO_3$ by boiling with mineral acids and that do not contain titratable ingredients which cannot be accurately titrated in water solution with methyl orange as the indicator.

### Apparatus

*General*:

2. The apparatus shall consist of a glass flask provided with a glass stopper and an air condener. The connection between the flask and the condenser shall be a ground joint. Perforated glass beads shall be used to prevent bumping.

*Flask*:

3. The glass flask (Fig. 1) shall be an Erlenmeyer flask made of Pyrex or other chemically resistant glass, having a capacity of approximately 300 ml.

*Condenser*:

4. The condenser (Fig. 1) shall consist of a glass tube having a length of 914 mm. (36 in.) and 8 mm. (5/16 in.) outside diameter. The lower end of the tube shall be flared and ground to fit the mouth of the Erlenmeyer flask.

*Glass Beads*:

5. The glass beads shall be perforated, made of chemically resistant glass, and shall be approximately 4 mm. (5/32 in.) in diameter. Before use, the glass beads shall be boiled thoroughly in several portions of water or until the wash water reacts neutral to methyl orange indicator.

### Reagents

*Alkali*:

6. The alkali shall be normal caustic soda, standardized according to good practice.

*Acids*:

7. The acid shall be N/2 sulfuric and approximately normal sulfuric acid. The former standardized according to good practice.

*Ether*:

8. Ethyl ether U.S.P. shall be used as the solvent.

*Sodium Chloride*:

9. The sodium chloride used shall be C.P. and neutral to methyl orange.

*Methyl Orange*:

10. A 0.1% water solution of methyl orange shall be used as the indicator.

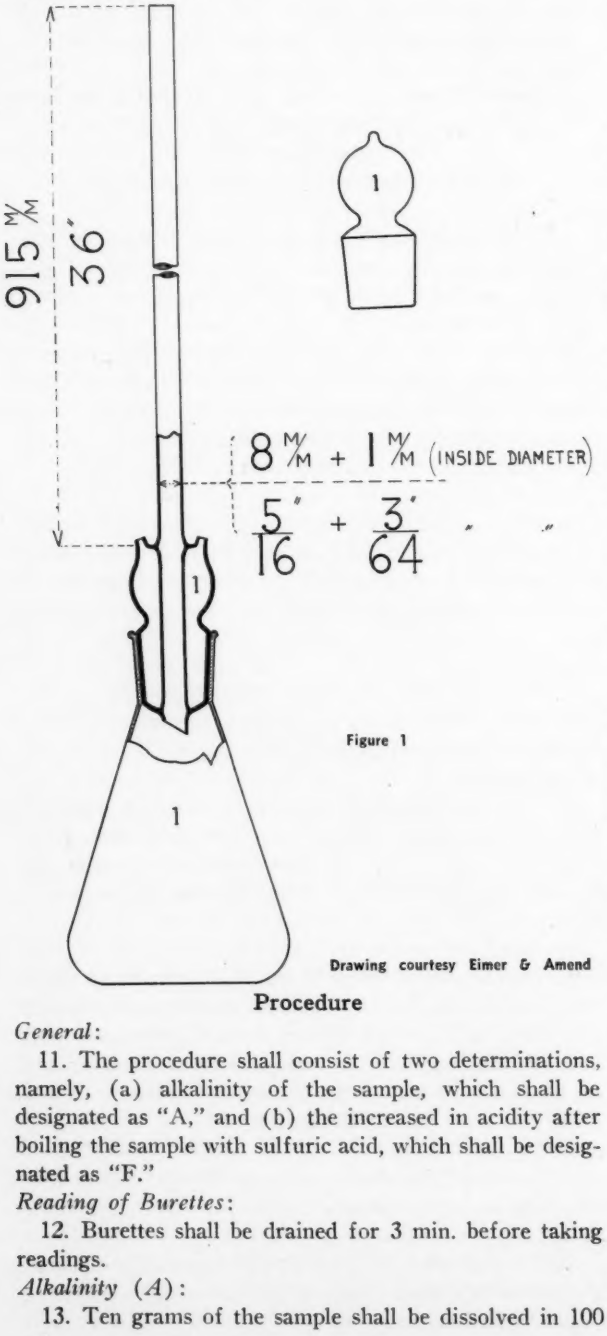


Figure 1

## Procedure

*General*:

11. The procedure shall consist of two determinations, namely, (a) alkalinity of the sample, which shall be designated as "A," and (b) the increased in acidity after boiling the sample with sulfuric acid, which shall be designated as "F."

*Reading of Burettes*:

12. Burettes shall be drained for 3 min. before taking readings.

*Alkalinity (A)*:

13. Ten grams of the sample shall be dissolved in 100 ml. of water contained in the Erlenmeyer flask, warming to obtain solution if necessary. Thirty grams of sodium chloride and 25 ml. of ether and 5 drops of methyl orange shall be added, and the mixture titrated with N/2 sulfuric acid. The flask shall be stoppered frequently during the titration and the contents well shaken.

14. The number of ml. of the acid multiplied by the normality of the acid and divided by the weight of the sample shall designate the alkalinity "A," or

$$A = \frac{\text{ml. } H_2SO_4 \text{ for titration X Normality of } H_2SO_4}{\text{Weight of Sample}}$$

*Increase in Acidity Upon Boiling (F)*:

15. Ten grams of the sample shall be weighed into the Erlenmeyer flask and boiled for 1 hour and 15 minutes under the air condenser with excess normal sulfuric acid, using glass beads to prevent bumping. The amount of sulfuric acid shall consist of the amount necessary to neutralize the alkalinity (A) of the sample plus 25 ml. in excess. The heating shall be so regulated that though boiling rather vigorously very little evaporation takes place. The contents shall be frequently agitated during the boiling. At the end of the heating period, the condenser shall be washed with a spray of water from a wash bottle, then disconnected from the flask and the contents cooled. Thirty grams of sodium chloride, 25 ml. of ether, 50 ml. water, and 5 drops of indicator shall be added, and the mixture titrated with N/1 caustic soda to the same end-point as in the total alkalinity titration. The flask shall be stoppered frequently during the titration and the contents well shaken.

*Blank*:

16. A blank shall be run simultaneously with the sample, using the same amount and strength of the sulfuric acid, approximately the same weight of glass beads, and heating and titrating under the same conditions as the sample.

*Calculation of "F"*:

17. The ml. of N/1 caustic soda required to titrate the sample minus the ml. required to titrate the blank, multiplied by the normality of the alkali and divided by the weight of the sample shall designate the increase in the acidity "F," or

$$F = \frac{\text{(ml. NaOH to titrate sample minus ml. NaOH to titrate blank) X Normality of the NaOH}}{\text{Weight of Sample}}$$

The increase in acidity (F) may be negative, in which case the sign shall be retained in the formula given under "Calculation."

## Calculation

*Organically Combined Sulfuric Anhydride*:

18. The algebraic sum of A plus F multiplied by 8 shall be the percentage of organically combined sulfuric anhydride, or

$$\% \text{ Organically Combined } SO_3 = 8\ (A + F)$$

and shall be reported as: ". . . . % organically combined $SO_3$ by weight, A.A.T.C.C. Sulfuric Acid Titration Method."

### Accuracy

*Accuracy*:

19. The accuracy to be expected with this method is that duplicate determinations of organically combined $SO_3$ shall not differ from each other by more than 0.05 ml. of normal solution, or equivalent to about 0.04% of combined $SO_3$.

## Proposed Standard Method of Test for Organically Combined Sulfuric Anhydride in Sulfonated Oils A.A.T.C.C. Ash-Gravimetric Method

*Scope*:

1. This method of test determines the organically combined sulfuric anhydride existing in a sample of sulfonated oil by dissolving the sample in a solvent, acidifying, washing with a saturated solution of salt, and ashing the purified extract. This method of test applies to all types of sulfonated oils, including those containing sodium acetate or similar titratable compounds.

### Reagents

*Ether*:

2. Ethyl ether U.S.P. shall be used as the solvent.

*Sodium Chloride*:

3. The sodium chloride shall be C.P. and used in a concentration of 25%.

*Sodium Sulfate*:

4. The sodium sulfate shall be C.P. and used in a concentration of 25% (anhydrous).

*Methyl Orange*:

5. A 0.1% water solution of methyl orange shall be used as the indicator.

### Procedure

*General*:

6. The procedure shall depend upon whether or not the sample contains ammonia.

*In the Absence of Ammonia*:

7. Five to eight grams of the sample—depending upon the concentration of fatty matter—shall be weighed into a 250 ml. pear-shaped separatory funnel containing 50 ml. of sodium chloride solution, 5 drops of methyl orange indicator, and 75 ml. of ether. The mixture shall be shaken and neutralized with approximately normal sulfuric acid until the lower layer is distinctly pink (0.2 ml. excess). If an emulsion forms, 2 ml. of alcohol shall be added at a time until the emulsion breaks, mixing gently after each addition of alcohol. After settling the lower layer shall be drawn off into another separatory funnel and the ether layer washed with 20 ml. of the sodium chloride solution. The water layers shall then be combined and extracted with 2-20 ml. portions of ether. The ether extracts shall then be added to the ether layer in the first funnel, any water that may settle carefully removed, and the combined ether layers shaken well with 10 ml. of the sodium sulfated solution at 40° C., for 3-5 minutes. After settling the lower layer shall be removed as completely as possible, warming it in warm water or with steam should the salt tend to crystallize. The ether layer shall now be cooled to about 15° C., if necessary, the inside wall of the funnel scratched with a glass rod to induce crystallization of traces of salt, and finally filtered into a dry 250-c.c. Erlenmeyer flask. The separatory funnel and crystals, if any, shall be washed with 3-10 c.c. portions of ether or until free from fatty matter. The ether solution shall now be immersed in ice water for 15 minutes, warmed with little stirring to 25-30° C. to bring back into solution any fat that may have separated, allowed to settle, and filtered immediately into a dry 300 ml. flask. The flask and filter paper shall be washed with 5-10 ml. portions of ether or until free from fatty matter. The filtered ether solution when again chilled to 0° C. and then warmed to room temperature shall remain perfectly clear.

The ether solution shall be evaporated until the volume has been reduced to about 20 c.c. and the residue transferred to a tared 50-c.c. crucible (high form). The crucible shall be immersed in a 100-c.c. beaker filled with warm water, until practically all the ether has evaporated. The flask shall be rinsed with 2-10 ml. and 3-5 ml. portions of ether, respectively, or until all the oil has been transferred to the crucible, each addition of rinsing ether shall be made only after the ether of the previous portion has practically evaporated. The residue freed from solvent shall be gently burned and finally ignited to constant weight. To prevent creeping of oil and to hasten the evaporation, the solution may be stirred with a glass rod; before the oil is burned, the rod shall be wiped clean with ashless filter paper which shall be added to the crucible. To oxidize traces of carbon or sodium sulfide that might form, the ash shall be moistened with 30% hydrogen peroxide and again carefully ignited to constant weight.

*In the Presence of Ammonia*:

8. Five to eight grams of the sample shall be dissolved in 80 ml. of water in a 300-ml. beaker. Ten ml. of N/1 NaOH shall be added and the solution boiled gently until wet litmus paper no longer indicates ammonia. The solution shall now be cooled and transferred into a 300-ml. pear-shaped separatory funnel and about 35 grams of solid sodium chloride added, or enough to make finally a 25% salt solution. Five drops of methyl orange shall be added and the neutralization, extraction, etc., conducted as under "In the Absence of Ammonia."

### Calculation

*Organically Combined Sulfuric Anhydride*:

9. The weight of the ash divided by the weight of the sample multiplied by 100 shall be the percentage of extracted ash in the sample. The per cent extracted ash multiplied by 1.1267 shall be the percentage of organically combined sulfuric anhydride in the sample, or

Per cent combined sulfuric anhydride = 1.1267 times per cent extracted ash

and shall be reported as: ". . . . % organically combined $SO_3$ by weight, A.A.T.C.C. Ash-Gravimetric Method."

## Accuracy

*Accuracy*:

10. The accuracy with this method is limited to the losses due to manipulation. Practice has shown that the accuracy to be expected is that duplicate determinations of the ash should not differ from each other by more than 5 mgms.

## Acknowledgment

The chairman is greatly indebted to the members of the committee for their capable, willing and painstaking co-operation, and to Professor L. A. Olney for repeated encouragement during the progress of this work.

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**CALENDAR OF COMING EVENTS**

* * * *

**Meeting, N. Y. Section, combined with Annual Meeting of the Association, Chemists' Club, New York City, December 8.**

* * * *

Proceedings of the American Association of Textile Chemists and Colorists

# UNEMPLOYMENT REGISTER

Members of this association, who are without employment, should forward to the secretary a statement as to their qualifications and experience. This information will subsequently appear on these pages with an identifying key number. Employers are also requested to file with the secretary any vacancies which may occur in their businesses.—A. Newton Graves, Secretary, care Franklin Process Company, Providence, R. I.

**Key: A—Laboratory and research; B—Dyeing or printing; C—Finishing; D—Sales; E—Instruction; F—Executive**

NOTE. Persons who have obtained employment should notify the secretary at once. Prospective employers may file vacancies either with the secretary or the AMERICAN DYESTUFF REPORTER.

**A-2**

*Education*—B.T.C., Lowell Textile Institute, 1932; also course in shorthand and typing.

*Experience*—None to date, interested in quantitative analysis, experimental dyeing, color matching, dye testing and dye identification. Ability to learn quickly and will go anywhere. 23 years old, single.

**A-B-2**

*Education*—Lowell Evening Textile School, 1917.

*Experience*—Five years' experience in hosiery dyeing, full fashioned hosiery of silk and cotton and silk, also men's hosiery containing rayon, wool, cotton and celanese. Several years experience in laboratory work. Has also had experience in jig-dyeing of cotton piece goods, slub and top dyeing.

**A-E-2**

*Education*—B.T.C., Lowell Textile Institute, 1933.

*Experience*—Assistant instructor in chemistry, Lowell Textile Institute. Member of scholastic honorary fraternity.

**A-B-C-1**

*Education*—Graduate Industrial Chemical Engineer, Pratt Institute—1911.

*Experience*—One year as plant control chemist, 4 years as laboratory chemist with gas company, 13 years as plant chemist with bleaching, dyeing and finishing plant. (Rayon and cotton piece goods). Formulated processes and put them into plant operation, 1 year as chemist and demonstrator for dyestuff company, 1 year as superintendent colorist with print works printing linen and rayon, 1 year as director of testing laboratory for national dry goods concern.

**A-B-E-1**

*Education*—B.S. in chemistry at C.C.N.Y. Working now on M.A. at Columbia.

*Experience*—7 years as dye tester and color matcher for dye manufacturer; 6 months skein silk and rayon dyer; 4 years textile chemist and dyer for cotton finishing concern; 2 months boss bleacher and 4 years as teacher of organic chemistry and dyeing. Age 38, single.

**A-E-1**

*Education*—Ph.D., Univ. of Illinois, studied chemical engineering at Columbia, licensed chemical engineer, New Jersey.

*Experience*—10 years' experience teaching in colleges, subjects included chemical and textile subjects. Has had broad experience in industrial work including experience in testing materials, research and consulting. Will go anywhere; references.

**B-1**

*Education*—Educated and trained in chemistry and calico printing in Glasgow, Scotland.

*Experience*—Has been with large print works as colorist for 13 years producing first class work on cotton, rayon, wool and silk fabrics. References.

**B-2**

*Experience*—Boss dyer with one firm for 18 years, divisional supt. at print works for 1 year, in charge of processing and dyeing of cottons and rayons at large bleachery for 6 years. Prefers bleachery in East but will go anywhere. References.

**B-3**

*Experience*—Foreman piece dyer for the past 21 years. Can dye the following; celanese, rayon, cotton lacks, wool, silk and mixed fabrics. Has knowledge of finishing and laboratory work.

**B-6**

*Education*—Graduate R. I. School of Design.

*Experience*—5 years in bleachery, 7½ years as assistant dyer, 2 years as boss dyer and 3 years as superintendent of dyeing and finishing. Married, 33 years old. References.

**B-7**

*Experience*—4 years as assistant to manager in ribbon mill; 2 years as boss dyer on veils, chiffons and silk skeins; 5 years as boss dyer on ribbons and skeins (cotton and silk); 7 years as boss dyer on spun silk (pure dye and fast) resisted colors; last 12 years as hosiery dyer on silk and cotton, silk-cotton, rayon or wool. 50 years old, married. References.

**B-8**

*Education*—Chemistry and Dyeing Department, Philadelphia Textile School.

*Experience*—Eleven years experience as chemist and boss dyer on the following: woolen, worsted and cotton yarn; woolen, worsted and union piece dyes on both ladies and men's wear; wool, cotton, shoddy and mohair raw stock. Age 33, married, will go anywhere. References.

**B-9**

*Experience*—Hosiery dyer with fifteen years' experience on high grade silk hosiery; familiar with all types of machines. Age 43, married. Will go anywhere. References furnished.

**B-10**

*Experience*—Ten years in top dyeing for fancy men's wear trade, knitting trade and sports wear; also piece dyeings on men's wear, crepes, sports flannels and tropical suitings; also several years association with commission dyeing trade doing tops, worsted skeins, cotton skeins, piece dyes, peroxide bleaching, naphthols, mohair plushes and imitation caracul cloths. Familiar with many types of machines. 38 years old, single with dependents. References.

**F-1**

*Education*—Textile Institute, Alexander Hamilton Inst., Extension work at Brown Univ., working knowledge of German.

*Experience*—Has had executive departmental work with all types of textiles manufacturers. Acquainted with all types of textile machinery, dyestuff application, laboratory practice, cost methods, and checking methods and processes. References.

## APPLICANTS FOR MEMBERSHIP

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## LEISURE AND SHORTER HOURS

TWO recent news items, more or less connected, have recently appeared in the daily newspapers. One is the announcement of a program for the proper development of leisure under the hours of the NRA and the other is the control of jobs through scientific planning. It is rather ironic that plans are being made to improve the leisure time of the working classes while at the same time millions of unemployed are still trying to get work. The only solution that we see to the whole problem is to have still shorter working hours than are now in effect—thus creating equal leisure for all. This would mean that instead of having a forty hour week we would need a universal 35 or 30 hour week.

The committee working on the development of leisure for New York City declared that it had no intention of prescribing how others should spend their new leisure but it would be glad to point out to those who may be interested where they can pursue hobbies that they care to develop and to acquaint others about the educational and recreational facilities which now exist.

In regard to scientific planning of job control the Personnel Research Federation is planning to conduct a survey on occupational distribution. Charles S. Slocombe, associate director of the Federation has pointed out that employment in basic industries such as farming and mining, manufacturing and transportation have increased but 6 per cent since 1910, although production increased by 86 per cent. Mr. Slocombe then goes on to say:

"In actual fact, an 86 per cent increase in the quantity of goods consumed by a 35 per cent greater population was grown, made and transported by but a 6 per cent increase in workers. No less than 5,000,000 people found employment in financing, selling and trading in these goods, and in managing and administering all the private and public business of the country. It was in these groups that the greatest increase in workers took place. The total number so occupied increased by 81 per cent.

"The group of workers engaged in trade by present indications should continue to increase probably even more than the administrative group. The group of workers concerned with rendering service to these other workers has grown by 50 per cent. A population which has increased by 35 per cent has required an increase of 50 per cent in the number of people serving it. This 50 per cent increase, moreover, has all occurred since the war, so this group shows the fastest growth."

Mr. Slocombe further indicated that the shortening of working hours should offset the increased tendency to divergence and bring the number of wage earners back more nearly into direct relationship with the quantity of production. He also stated that not only must declining industries be watched but the number of people entering growing industries should be controlled as even the fastest growing industries cannot give jobs to an unlimited number of people. It is expected that in this way it will be possible to plan for future employment so that there will not be too many workers in one field and too few in another.

Going back to the committee planning on the proper development of leisure the question naturally will be asked why it is necessary or advisable to have such planning. A person without work is more interested in filling his pockets with money and his stomach with food than he is in improving his mind, etc. On the other hand a person who has a job generally knows what he wants to do with his leisure time and acts accordingly. In such cases the plannings of the committee would probably have no value but as explained by the committee its object is to help evolve a program of educational, recreational and other useful activities for the consideration of industrial workers who have benefitted or will be benefitted from the increased leisure hours at their disposal as a result of reductions in working hours. The real working of this committee will be to provide the facilities for the use of people who do desire them for their leisure. It will provide additional educational and cultural facilities for people who otherwise would not have them and who earnestly desire them.

And so, with such committees as the two mentioned above it looks as if the life of the worker at some time in the future will be rosy indeed . . . when they all have work combined with plenty of leisure.

## Annual Meeting U.S.I.T.R.

The fourth annual meeting of the United States Institute for Textile Research, Inc., was held on Thursday, November 2nd, at the Hotel Commodore in New York City.

A symposium on "The Status and Correlation of Current Textile Research in the United States" was held, Dr. Vannevar Bush acting as chairman. Discussion was led by Ephraim Freedman, Robert E. Rose and H. DeWitt Smith.

The following directors were re-elected by the corporation for a three-year term Jno. W. Arrington, Pres., Union Bleachery, Greenville, S. C., Thos. T. Clark, Pres. and Treas., Talbot Mills, North Billerica, Mass., D. F. Edwards, Pres., Saco-Lowell Shops, Boston, Mass., H. Grandage, Vice-Pres., Clark Thread Co., New York, N. Y., K. P. Lewis, Pres. and Treas., Erwin Cotton Mills Co., Durham, N. C., Albert R. Pierce, Agent, Pierce Mfg. Corp., New Bedford, Mass. Robert R. West, Pres. and Treas., Riverside & Dan River Cotton Mills, Danville, Va., was succeeded by H. M. Chase, supt. and tech. director of the same company. A. L. Lustig, Pres. and Gen. Mgr., Apponaug Co., Apponaug, R. I., was elected for the same term, succeeding W. Robert Blum, resigned.

All officers were re-elected with the exception of W. Robert Blum as vice-president, he being succeeded by Alban Eavenson, Pres., Eavenson & Levering Co., Camden, N. J.

Membership of the Research Committee was increased by election of Alban Eavenson, president of the Eavenson & Levering Co., Camden, N. J., and Philip A. Johnson, Pres. and Treas. of the Aspinook Co., Jewett City, Conn. Dr. H. DeWitt Smith, Treas., A. M. Tenney Associates, was elected vice-chairman of the research committee.

Among the new members elected to contributing membership in U. S. Institute were: The Clark Thread Co., Newark, N. J., and J. & P. Coats (R. I.) Inc., Pawtucket, R. I., represented by H. Grandage, vice-president.

The following were elected to annual membership in U. S. Institute: American Printing Co., Fall River, Mass., auth. rep., J. R. Bonnar, Technical Director; Chatham Mfg. Co., Elkin, N. C., auth. rep., T. M. Roth; LaWall & Harrisson, Philadelphia, Pa., auth. rep., Jos. W. E. Harrisson; Mrs. Ellen B. McGowan, Teachers College, Columbia Univ., New York City; Mr. E. A. Milne, Griswoldville Mfg. Co., Griswoldville, Mass.; William H. Porcher, Southern Agent, Whitin Machine Works, Charlotte, N. C.; Robert L. Sibley, Mgr., Development Dept., Rubber Service Laboratories Co., Nitro, W. Va.; Skenandoa Rayon Corp., Utica, N. Y., auth. rep., F. W. Mattinson; The Twining Laboratories, Fresno, Cal., auth. rep., F. E. Twining; Mr. Ivan Wolff, Business Engineers, Inc., New York City.

## Corrosion in Sulfonators

Corrosion tests have been made at the plant of Endicott Johnson Corporation in cooperation with the International Nickel Company to establish the behavior of metals in sulfonators under actual operating conditions. The specimens insulated from one another were fastened on a spool type specimen holder, that was submerged within the sulfonator.

In the first series of tests the specimens were exposed during the sulfonation of 10 batches of neatsfoot oil by a process in which 66° Baumé sulfuric acid was added to the oil over a period of about one hour after which the reaction proceeded for about six hours at a maximum temperature of 34°C. At the end of six hours a saturated sodium chloride brine was added to the mixture, which was then thoroughly agitated and allowed to settle over night, after which the sulfonated oil was drawn off.

In the second series 66° Baumé sulfuric acid was allowed to react with cod liver oil over a period of about six hours after which a 15% sodium chloride brine was added and agitated as in the first case, allowed to settle over night and then drawn off. In this case the oil was finally neutralized with alkali.

Corrosion rates were as follows:

| | *Corrosion rate-mg. per sq. dm. per batch* | |
|---|---|---|
| *Metal* | *Sulfonated neatsfoot oil* | *Sulfonated Cod liver oil* |
| Lead | 127 | 165 |
| Chromium-nickel iron (18-8) | 425 | 22 |
| Nickel | 30 | 25 |
| Monel Metal | 34 | 11 |
| Ni-Resist | 90 | 29 |
| Plain Cast Iron | 10,000 | 120 |

## New National Dye

National Alizarol Cyanine RC is an addition to the National Aniline line of mordant dyes. This product is said to give a bright reddish blue of excellent fastness to sea water, perspiration and rubbing, and of good fastness to washing, fulling, potting, cross dyeing and alkali spotting. It is also said to possess fair fastness to light but its other properties are said to merit its use alone or in combination on raw stock, yarns and pieces for a variety of purposes. Cotton, rayon and acetate silk effects are unstained.

## Family Welfare Committee

Mr. Harry L. Derby, President of the American Cyanamid & Chemical Corporation, has become a member of the Executive Committee of the Family Welfare Committee's campaign to raise $4,000,000 to help New York City's family relief agencies.

Mr. Derby, as Chairman and Mr. J. L. Schroeder, as Vice-Chairman, of the Chemical and Paints Group of the Gibson Committee, with the assistance of a committee of twenty-two leading representatives of the industries, last year raised $117,000 for unemployment relief. The work of soliciting the industry was carried on with such vigor and success that they were asked by the Family Welfare Committee to act in the same capacity this year.

## RAYON DYEING AND FINISHING

(Continued from page 694)

As satin fabrics must be handled as gently as possible in the wet treating operations and should be "wet processed" as quickly as is compatible with the production of the desired results; yarns entering these fabrics should be sized with materials that are easily and quickly removed by the scouring operation. By the same token, the dyer should determine the type of warp size used and should then so constitute the scouring bath that the sizing material is removed with the minimum amount of mechanical handling of the fabric.

Many of the crepe back rayon face satins present very serious processing difficulties to the dyer due to the presence of tightly twisted gum silk in the filling. Indeed, few finishing plants can properly handle such fabrics even today. The necessity for close cooperation between the dyer and the fabric manufacturer is more pronounced in the case of crepe back satin fabrics than in any other fabric construction. Minor changes in fabric construction sometimes enable a dyer to successfully obtain the desired result in a good crepe back satin effect.

The dangers of twist variations and tight warp threads, discussed under flat crepes, are even more pronounced in the case of the crepe back satins.

### Pile Fabrics

The only fabric we will consider under this heading is the well known transparent velvet. The various novelty effects, such as fancy etched pile fabrics, etc., come under the heading of specialties and will not be discussed here.

The pile yarn used in pile fabric constructions contains only slight quantities of sizing material which are readily removed by mild processing. The backing yarns of transparent velvets often consist of gum silk which obviously require a lengthy scouring procedure.

The dyer should carefully notice the condition of the pile before processing as it sometimes happens that the pile is so woven that an erect pile cannot be produced by the usual dyeing and finishing methods.

### Acetate, Acetate and Rayon, Acetate and Cotton Fabrics

Acetate-containing fabrics will be found in all of the above-discussed constructions. Regardless of the scouring baths and procedures that should be used in the proper processing of these fabrics, it is esential that they be handled below the temperature at which the particular acetate involved becomes delustered (unless a piece delustered fabric is desired).

Particularly when the acetate is present as a warp yarn, gelatine and casein sizing materials are very apt to be found. The use of protein destroying enzymes in conjunction with the scouring of these fabrics often proves advantageous and should be more widely used.

### Acetate and Real Silk Combinations

Fabrics containing acetate rayon and gum silk present a most serious problem from the scouring viewpoint. Whereas the silk gum should be removed at or just below the boil, the acetate yarn prevents the dyer from going above 180° F. without serious danger to the acetate yarn. The only material that need be considered as an impurity from a scouring viewpoint in these fabrics is the silk gum, as a scouring procedure drastic enough to remove the silk gum will effectively remove such other impurities and sizing materials as may be present.

### Specialties

The various specialty fabrics, such as novelty Shantungs, tie silks, scarfs, etc., must of necessity be handled by procedures especially adapted to produce the desired result in each instance. Only in a very few instances do these fabrics contain foreign materials other than those already considered in the foregoing discussion.

## DISCUSSION OF MACHINERY

### Dyeing Machines

Boil-off tubs are large wooden vats, the dimensions of which vary considerably from plant to plant and within individual plants depending upon the type of fabric handled. Most boil-off tubs are four feet wide, six to ten feet deep and twelve or more feet long.

Although certain types of fabric must be strung from the selvedges before immersion in the boil-off tub, most fabrics are wound into large skeins which are suspended from sticks placed horizontally across the tub.

Dye kettles, consisting of an oval shaped power driven reel, with a smaller wheel in front, which may or may not be power driven, and a wooden or monel metal tank which contains the dye liquor, are found in all plants processing rayon piece goods. A more complete description of these kettles will be found in Chapter VI of this series.

The old type of jig is so well known as to need no further description or discussion here. The newer ball bearing and special drive jigs have proven so advantageous in the handling of light weight rayon and rayon-containing fabrics that many plants have installed them.

The construction and operation of open string washers is so well known that a detailed description is unnecessary. These machines are built so heavy and rugged that they are not suitable for processing sheer fabrics. As a matter of fact, most rayon fabric are processed in machines other than string washers.

Open width washers vary greatly from plant to plant, presumably because of the variations in fabrics handled. Open width washers handling rayon should process sufficient power driven rollers and sufficiently free running friction driven rollers to keep tension low.

Practically all plants have on occasion designed and built special machines for the production of special results and to facilitate handling under conditions with which they are confronted. Many of these special machines have proven particularly advantageous for the wet processing of sheer rayon fabrics. Unfortunately, these machines cannot be discussed or described here.

### Extractors

Most rayon and rayon-containing fabrics can be satisfactorily handled in the ordinary type of centrifugal extractors.

The new rotary extractor has proven particularly well adapted for removing the water from sheer rayon and rayon containing an easily injured face.

Some plants have used vacuum extractors to good advantage for removing the surplus water from the types of rayon-containing fabrics that must be handled in the flat state throughout the entire wet processing operations.

### Dryers

Loop dryers continuously hang damp fabric in loops on an endless belt of slats that carries the loops slowly through a heated chamber that is continuously supplied with preheated air. These dryers are used for preliminary drying (after dyeing and before finishing) of practically all flat fabrics.

This type of dryer allows fabrics to shrink to the maximum degree as no tension is applied to warp or filling during the drying operation. It consists of a series of endless belts that carry fabric back and forth through a chamber continuously supplied with preheated air.

It is especially adapted to drying "georgette" crepes and related fabrics. In fact its use for the drying of georgette, has become so universal that the machine is usually referred to as a "Georgette" Dryer.

A large proportion of all flat rayon and rayon-containing fabrics are dried during the finishing operations on tenter frames. These frames consist of two parallel rows of moving clips or pins so designed and arranged that the fabric is automatically and continuously grasped, held, and conducted over a source of heat while in an extended condition. The frames are so constructed that they can be adjusted to any desired width or widths at either end.

Depending upon the results desired, and the fabrics processed, these frames are heated by means of steam pipes or gas flames placed a short distance under the fabric and at various locations throughout the length of the frame.

The operation of a pin tenter frame is extremely obvious. Clip frames contain a great number of small moving parts operated by cams at both ends of the frame in such a manner that these moving parts firmly grasp the fabric as it feeds into the frame, hold it firmly throughout its traverse, and automatically release it at the further end of the frame.

Particularly in finishing plants primarily designed to handle cotton fabrics, drying cans are used for removing the moisture from wet processed rayon and rayon-containing fabrics. These "cans" consist of large hollow copper cylinders heated from the inside by means of steam or gas, and so arranged in series that the treated fabric comes in contact with one-third or more of the surface of the entire series of cans. When rayon warp fabrics are processed, the surface speed of the cans must be so adjusted that the last can to come in contact with the goods moves appreciably slower than the first can. Unless this precaution is taken, the natural shrinkage of rayon during the drying operation will cause so much tension to be applied to the fabric that the fabric must be torn, stretched unduly, or given a high polish (due to slippage between the final cans and the fabric surface).

The well known Palmer calender is used in the finishing of rayon and rayon-containing fabrics other than crepes, when a soft pleasing hand is desired, and when the fabric will stand the extra cost of Palmering. The Palmer consists of a fabric spreading device, a crutch for the application of finishing materials, a preliminary drying device (steam coils or gas flame) and a very large internally heated, slowly revolving copper drum covered with a soft endless belt consisting of a felt fabric. The fabric is slowly dried while held between the revolving drum and the endless belt.

Goods finished on the Palmer machine have a very pleasing soft full hand.

### Wet Finishing Machines

The term "crutch" has been applied to wet treating machines consisting of two or three rollers, the bottom one of which is partially immersed in a tank capable of containing liquor. Crutches are usually used in conjunction with other machines, such as georgette dryers, tenter frames, etc. They are usually preceded by a fabric opening device of some sort in order that wrinkles may not enter the nip of the rollers. The rollers are made of a variety of materials and are often covered with various sorts of cloth in order to impart the desired amount of squeeze and liquor to fabrics processed.

A spraying machine consists of a means of opening fabric to be treated, a fine spray located above the fabric in such a way that a mist containing the desired finishing materials is allowed to settle on the surface of the fabric, and a rolling device so designed that the fabric can be rolled up with heavy paper. This machine is used for the application of special finishes to the surface of fabrics that cannot be "wet processed" in the ordinary sense of the term without the loss of the crisp hand sometimes desired, as for example, in tight woven fine denier taffetas. Such fabrics when processed on the spraying machine are given the required amount of firmness and are pressed into a smooth pleasing appearance by the means above described.

In addition to the above described finishing machines there are many special machines, each of which was originally designed to handle some particular specialty fabric, and which have been adapted for certain of the standard fabrics by the plants in which they are located. Unfortunately, these special finishing machines cannot be discussed here.

### Dry Finishing Machines

When cost permits, and when a particularly smooth finish is desired, woven fabrics, other than crepes and pile fabrics, are processed on calendering machines. A calender is essentially an ironing machine consisting of

two or more large rollers revolving against each other, to which extremely heavy pressures may be applied. The machines are so arranged that each individual roller can be driven at the same, or at differing speeds, as desired. The rollers are made from a great variety of materials, but are usually so arranged that a hard roller always revolves against a relatively soft roller. The so-called soft rollers are actually very hard and are soft only when compared with iron or steel.

Palmer machines accomplish a drying and finishing operation simultaneously. These machines have been considered under the heading of dryers.

Fabrics processed upon drying cans, tenter frames, and calenders usually have a "boardy" rather than a "lofty" hand. When it is necessary that such fabrics be given a relatively "lofty" hand, it is necessary to process them on a breaking machine. These machines overcome the "set" condition imparted to fabrics by the above mentioned drying and finishing machines.

The most popular of the breaking machines is the so-called button breaker. This machine consists of a series of rollers in which have been set a large number of small smooth, projecting nubs. The fabric is slowly drawn through the machine in such a way that it contacts with 1/3 or more of the surface of each of these rollers. As the fabric is slowly drawn through the machine, the rollers are revolved at a high rate of speed, thus accomplishing a beating and shaking action which effectively breaks up the "set" of the goods.

Certain fabrics, such as transparent velvets, must be given a shear treatment in order to properly prepare them for market. A shearing machine consists of a large revolving cylinder containing many curved knife blades and a stationary member that resembles a knife edge, over which the fabric is slowly drawn during the shearing process.

Fabrics containing cotton or other spun yarns, and which present a fuzzy appearance in the finishing room, are processed through a singeing machine which consists of a series of gas flames so arranged that they burn the fuzz from the face and back of fabrics when the same are drawn rapidly through the machine.

In some instances a curved copper plate heated to red heat replaces the usual gas flame.

Whereas inspection machines do not properly come under the heading of finishing machines, they are important enough to deserve special mention here. Most plants are equipped with inspection devices so arranged that the fabric can be inspected by light from a northern exposure.

After inspection most flat woven fabrics are processed on rolling or folding machines. The rolling machine is a simple device for rolling the fabric on a cardboard tubing. The folding machine doubles the fabric once and rolls it upon a flat wooden or cardboard rectangular board. Fabrics that are imperfectly rolled or folded acquire wrinkles and creases during storage. These imperfections are practically always blamed upon the dyeing and finishing operations by the firms to whom the same are sent. Trouble from wrinkles and creases imparted by rolling and folding machines are absolutely unnecessary and should be avoided.

## METHODS OF SCOURING, DYEING AND FINISHING RAYON AND RAYON-CONTAINING FLAT WOVEN GOODS

### Flat Crepes

Rayon flat crepes fabrics are rarely ever desized prior to the scouring operation as it is generally assumed that scouring baths should remove all trace of size. The desizing is resorted to only when absolutely necessary to give the fabric a satisfactory hand.

Many flat crepe fabrics that are not at present given a desizing treatment would be materially improved with respect to hand if given a preliminary desizing operation.

When desized, flat crepes are usually processed in the desizing liquor for one to two hours at 100-130° F. in a silk boil-off tub or similar apparatus.

The desizing liquor usually contains a large excess of starch destroying enzymes over the theoretically necessary amount with or without the addition of a small quantity of protein destroying enzymes.

In some instances (when boil-off tubs are not available) the desizing is done in dye kettles—the fabric being soaked overnight in the desizing liquor.

Flat crepe fabrics should be scoured in silk boil-off tubs as this method of handling allows properly designed flat crepe fabrics to slowly shrink without distortion of the warp threads.

Fabrics scoured by the "boil-off" method are suspended in skein form and are worked in the hot boil-off liquor for a period of one to three hours. At the end of the boil-off period, the fabrics are rinsed in a separate tub and are carried to the dyeing machine for further processing.

For the sake of economy large quantities of flat crepe fabrics are boiled off in the dye kettles. This procedure is the same as that described under the scouring of circular knitted fabrics in Chapter VI.

This method of scouring flat crepe fabrics, although economical, should rarely be resorted to, as it allows the warp threads to shift in most of the flat crepe constructions. Flat crepes scoured "in the kettle" are decidedly inferior in appearance when compared with those scoured by the "boil-off" method.

Flat crepe fabrics are dyed in the reel type of dye kettle in exactly the same manner as are circular knitted rayon fabrics (Chapter VI). This operation is so common and well known as to need no further discussion here other than to note that these fabrics must be dyed as rapidly as possible to prevent shifted warp threads.

Flat crepes are extracted in the usual manner and are dried in the loop type of drying machine.

Flat crepes are prepared for the printing operation by running through a crutch and over the tenter frame, the tensions being determined by the specification given by the boss printer. Although in some instances a wetting-out agent is applied in the crutch, this practice is not general.

Finishing oils consisting of sulfonated olive oil with or without the addition of other oils and with or without the addition of glycerine or other deliquescent agent are usually applied to flat crepe fabrics by means of a crutch placed before the tenter frame. The fabrics are then tentered in the usual manner. Care must be observed in the tentering of flat crepe fabrics that proper tensions are applied both to the filling and to the warp as the appearance and hand of the finished fabric can very easily be materially altered on the tenter frame. The tension applied is usually determined by the customer rather than the finishing plants as the customer states the width of the finished fabric and the warp-wise shrinkage wanted.

When the customer is willing to pay for the added operation, and when a particularly soft finish is wanted, flat crepe fabrics are given several runs over a button breaker after the tentering operation.

The terrific variation in flat crepe fabric constructions, the variations in machinery available and in results wanted by different customers make it necessary that flat crepe fabric finishing procedures shall vary considerably from plant to plant and from fabric to fabric. The following procedure, successfully used during 1930, is typical, rather than a specific example:

**(All-rayon flat crepe, untwisted warp, heavy twisted filling—left and right twist)**

*Per* 100 *Pounds*

(1) Prepare fabric for boil-off tub.
(2) Raise boil-off tub to boil. (Tub contains standing soap bath, the concentration being much greater than that necessary to process a single batch of fabric.)
(3) Shut off steam.
(4) Enter goods and work gently for two hours.
(5) Transfer goods to rinsing tub.
(6) Load goods into dye kettle.
(7) Dye in the usual manner. (Note: Dischargeable colors are used, as many rayon flat crepes are printed by the discharge method after the dyeing operation.)
(8) Rinse.
(9) Extract.
(10) Dry in loop dryer.
(11) Run through crutch containing softening solution (sulfonated olive oil) and continuously on tenter frame.
(12) Give six passes over button breaker.
(13) Inspect and pack for shipment.

### Voiles and Georgettes

Although some of the coarser voile and georgette fabric constructions are scoured on the dyeing machine, this practice results in the production of inferior fabric (chafe marks, etc.), and should never be resorted to. Rayon voiles and georgettes should be scoured in boil-off tubs or similar apparatus so designed that fabric is moved very gently during the scouring operation.

Voiles and georgettes are dyed on the reel type of machine in the same manner as are flat crepe and circular knitted rayon fabrics. As in the case of flat crepe fabrics, the dyeing operation should be so designed that the fabrics are processed in a reasonably short time. Dischargeable dyestuffs only should be used, as most voiles and georgettes are discharged printed after the dyeing operation.

Voile and georgette fabrics are scoured on the loop drier in the usual manner.

Voiles and georgettes are prepared for the printing operation by running through a crutch and over the tenter frame, the tensions being determined by the specifications of the boss printer. Although in some instances a wetting-out agent is applied to the fabrics simultaneously with the tentering operation, the practice is not general.

Voile and georgette fabrics are run through a crutch, the bowl of which contains a finishing oil usually consisting of sulfonated olive oil (with or without other additions, such as other oils and deliquescent materials) after which they are run continuously in to a georgette drier which allows the maximum shrinkage to be obtained.

From the georgette drier, the fabrics are taken to the tenter frame where they are steamed and tentered to the desired finished width.

Although a georgette construction would appear to preclude the practice, many voile and georgette fabrics are given a heavy calendering treatment in order to impart a pleasing soft hand.

The soft full hand of the Palmer finish is sometimes desired on voile fabrics. When such is the case, the fabrics are taken from the loop drier directly to the Palmer where they are continuously softened (sulfonated olive oil, etc.), dried, and calendered. This practice is not as general as is the georgette drier, steam tenter, calender procedure.

As in the case of flat crepe fabrics, the procedures for finishing voiles and georgettes vary so greatly from plant to plant and from fabric to fabric within the same plant, that the compilation of the various procedures used, and reasons for the variations, would be unnecessarily detailed and boresome. The following procedure is typical of voile and georgette finishing procedures:

### PROCEDURE

#### Voile and Georgette Fabrics

*Per* 100 *Pounds*

(1) Skein for boil-off tub.
(2) Raise boil-off tub to boil.
(3) Enter fabrics into boil-off liquor.
(4) Work gently for two hours.
(5) Rinse in separate boil-off tub.
(6) Move fabrics in dye machine.
(7) Apply color as rapidly as possible on reel type of dyeing machine.
(8) Extract and dry on loop drier.
(9) Apply finishing oil (sulfonated olive, etc.), on crutch, and run fabric continuously in the georgette drier.

(Continued on page 716)

## THE PRODUCTION OF VAT DYES ON PIECE GOODS

(Continued from page 688)

standing forty-eight hours, Orange 2RTS will not develop its true shade for several hours, all greens have a tendency to blue up on finishing, and so on. Finishing does of course tend to leave goods apparently very much thinner in shade than before. Beetling, calendering, shreinering and such all play their part and the result is that certain goods may easily look twenty per cent thinner by the time they reach the making-up room. To emphasize all this a full piece of cloth always looks a sight worse than a small pattern. On the other hand, many cloths require little or no finishing and it would be obviously folly to purposely leave on the full side. The vat dyer's lot is not an easy one, and adjustment of such matters as these has probably given me far more worrying hours than any other point in connection with vat dyeing.

### Choice of Dyestuffs

Disregarding dyestuffs made in identical form by different manufacturers, we have a comprehensive range of well over a hundred useful anthraquinone dyestuffs. These have been divided and sub-divided according to various classifications, but the most general and useful divisions from the dyer's point of view is their method of application.

About eleven years ago, our dyestuff manufacturers gave individual dyeing instructions for each dyestuff placed on the market, but with such a number of colors as are now available, this procedure would not be very helpful. Below is a division of the three main groups as classified by I. G. Farbenindustrie Aktiengesellschaft:

### I. N. Dyeing Colors

These are hot dyeing colors, dyed with a relatively large amount of caustic soda and no salt. The correct dyeing temperature is 50°-60°C.

The chief members of this class are the blues and greens, but a more detailed list is as follows: Indanthren Yellow G, Indanthren Gold Orange G, Indanthren Orange 2RT, Indanthren Scarlet 2G, Indanthren Brilliant Violet 2R, Indanthren Dark Blue BO, Indanthren Navy Blues BRF, G and R, Indanthren Blues BC, GCD, 3G, 3GT, 5G, RS, Indanthren Brilliant Blues R and RCL, Indanthren Brilliant Greens, B, FFB, 2G and 4G, Indanthren Greens 2B, G, 2G and GT, Indanthren Grey 3B.

Individual colors, even of one particular class, do often require special conditions. Indanthren Yellow G, for example, is a particularly difficult dyestuff to oxidize and more than the normal amount of sodium bichromate or perborate is required.

### I. W. Dyeing Colors

These represent a range of dyestuffs dyed with less caustic soda but with the addition of Glauber's salt. The correct dyeing temperature here is 43°-50°C. For average batches, Glauber's salt to the extent of 10 lbs.-30 lbs. is added according to the depth of shade. Members of this class are: Indanthren Yellow 3GF, Indanthren Yellow 3R, Indanthren Golden Orange 3G, Indanthren Red FBB, Indanthren Red 2G, Indanthren Scarlet R, Indanthren Olive R, Indanthren Yellow Brown 3G, Indanthren Browns BR, G, 2G, 3GT, R and 3R, Indanthren Red Browns R and 5RF and Indanthren Grey BG.

### I. K. Dyeing Colors

Our third classification consists of the cold dyeing colors, dyed at a temperature between 20° and 30°C, with the addition of Glauber salt in quantities up to 45 lbs. according to the depth of shade. Some of the chief members are: Indanthren Yellow FFRK, Indanthren Yellow GK, Indanthren Golden Yellow GK, Indanthren Brilliant Oranges GK and RK, Indanthren Orange 6 RTK, Indanthren Pink FBBL, Indanthren Reds BK, 5GK and RK, Indanthren Brilliant Violet BBK.

Even with the very detailed classification given us by the manufacturers, it really tends to somewhat complicate matters from a practical standpoint, as it invariably happens that a certain shade can only be produced with a mixture of two colors, each of which is supposed to be dyed in a different manner. Some dyestuffs dye quite well under different conditions, but the practice of mixing dyestuffs of different groups is one that should be avoided wherever possible. Most of the IK dyeing colors may be satisfactorily dyed by the IW method, but not so in every case. Using unsuitable mixtures, the tendency will be to have one dyestuff rushing on the fiber, and the other having little effect.

### Padding Methods

From the foregoing notes on jig dyeing of vat colors, it will be readily appreciated that production is necessarily comparatively slow, and on this account, many efforts have and are still being made with regard to some form of bulk working.

The following padding method unquestionably gives very satisfactory results with pale shades and possesses the distinct advantage that there is no danger whatsoever of heavy edges or selvedges showing. Furthermore, given anything like good running, production should easily surpass that of jig dyeing.

The cloth is padded on a two bowl mangle with a reduction mixture similar to the following:

x pints Caledon Orange 2RTS )
x pints Oleine Anthraquinone Standard)
1½x pints caustic soda 90° Tw.
1½ lbs. hydrosulfite
make up to 45 gallons

### Oleine Anthraquinone Standard

4 gallon Oleine.
1 quart Anthraquinone 30% paste.

Immediately after leaving the nip, an air passage of about twelve yards is allowed and the goods are piled on a wagon and allowed to stand for some length of time.

The goods are then usually soaped on a rope-soaping machine or open soaper or on the jigs themselves. It may of course be sometimes necessary to transfer to the jigs with a view of slight adjustment to shade. It is rarely necessary to develop with bichromate or perborate of soda.

### Padding

Perhaps the most difficult problem now confronting the vat dyer is that of obtaining satisfactory penetration, particularly with heavy shades on heavy cloths. Of the hundreds of assistants, wetting out agents and the like that have been offered to us, it is quite safe to say that all are as good as useless where the question of complete penetration of say a dark navy is required on a linen. To obtain such, the only known method is by first padding on the unreduced color, reducing and topping-up to shade afterwards on the jigs.

The following represents a typical working recipe:

4 pcs. Wt. 110 lbs. Length 90 yds. Shade Blue 6.
12 lbs. Caledon Blue G.C.D.
8 ozs. Olive R. S.
3 pints penetrating assistant 40° C.

It is highly important that the dyestuffs are in a very fine state of division and on this account, it is customary to carefully grind up in a mill before placing in the stock bath, usually situated at the side of the machine. Powder brands are not easily dispersed into a fine paste, and on this account are not to be recommended. After mixing, the liquor should be strained before use. This mixing is sometimes assisted by the addition of a small amount of Gum Tragacanth, Tragon or one of these locust bean products now on the market. Sometimes blue is used.

The usual three bowl padding machine fitted with drying tins is generally employed, though it is often a practice to batch up immediately leaving the nip and transfer to the dyehouse. With certain shades, even with the most rigid attention to controlling the running of the machine, a tendency towards "paling-off" will be found. This is overcome by running the goods through the machine the reverse way, though allowance has to be made for this before starting.

This type of padding is by no means easy to carry out and is certainly very expensive. On the other hand, it certainly does give the required result so far as penetration is concerned.

### Stripping of Goods

In view of some of my previous remarks regarding the supreme fastness of vat dyestuffs, the term "stripping" of these colors may appear somewhat ironical. It is however true to state that no dyestuff yet invented is absolutely fast in the true sense of the word, and the very best of the Indanthren series always have some little weakness.

It is unfortunately undeniable that all dyers have at some time or another made mistakes, and while from the vat dyer's point of view, these can rarely be remedied successfully, there are instances where a partial stripping can be effectively carried out.

Little written guidance is available on this subject, and I am unfortunately unable to prepare in any detail even a summary of which dyestuffs will withstand a certain treatment and which can be successfully adjusted. The result of personal observation and acquaintance with the particular dyestuffs in use is perhaps the dyer's only guide.

When dealing with vat colors, my strongest and most emphatic advice if the goods have gone wrong in some way is never to attempt any stripping of any sort, unless the goods are absolutely hopeless and unsaleable. To strip a vat dyestuff on a cloth worth only a matter of a few coppers per yard would be folly. Far better and cheaper is it to sell the goods to a fent merchant, even at a lower figure than grey price.

### Reduction with Hydrosulfite and Caustic

A few odd color specks, "settled" marks and such minor faults can often be completely and satisfactorily remedied by a few ends reducing in hydrosulfite and caustic, oxidizing and soaping again. It is of course usual to get a patch out of the goods after the reduction and if necessary add a fraction more dyestuff. When working at a temperature above 50°C, there is a very grave danger that the dyestuff will decompose and one will be left with a flat muddy shade that can never be brought up to the required tone. This is especially evident with blues and greens.

On the other hand, where shades have come up too full, this procedure will not be very helpful and little actual dyestuff is removed. A more severe treatment is necessary and in such cases the goods are usually run for an hour or so in a very strong bath, such as:

5 lbs. hydrosulfite.
8 pints caustic soda.

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25 gals. divide over 8 ends at 55° C.

If the dyestuff is one that will definitely not decompose, then more color will be removed by working at the boil. With blues and greens and colors that easily decompose, the temperature is usually around 50°C. Along with this reduction mixture, it is frequently the practice to add soap flakes. The addition of perhaps half a gallon of pyridine will in many cases prove helpful, but it is most unpleasant working in any dyehouse where pyridine vapor is being evolved. Experiments have been carried out very extensively showing that many organic solvents are especially helpful in the stripping of vat colors, but it is unfortunate that their cost is so very high that they have no practical importance.

### Glucose Reduction

The use of glucose instead of hydrosulfite is usually cheaper and quite as effective. Glucose of course possesses the advantage that boiling will not decompose it as does hydrosulfite.

It is interesting to observe that the addition of finely

powdered carbon or soot is often very helpful. An absolute thorough soaping is however required afterwards, and unless care is taken, dirty spots will easily be left on the goods.

### Oxidation Discharge

The use of permanganate of potash sometimes forms a favorite method of dealing with menders. The practice is to either pad or run the cloth through an acidified bath of permanganate of potash at the strength of 1/16-½ oz. per gallon. The goods are afterwards "cleared" with boiling oxalic acid or sodium bisulfite and thoroughly washed. It will be realized that this process has a very deteriorative action on the cloth and must on no account be practiced if there are any signs of weakness. It is important to see that all crystals have dissolved and the solution carefully strained before placing in the jig or padding box. Undissolved crystals will cause local tendering where they meet the cloth.

### Few Practical Difficulties Experienced

It would be somewhat of a task to enumerate many of the difficulties and little practical points confronting a dyer. Much depends to a very great extent on the local conditions. What can be carried out in one dyehouse cannot always be repeated in another. In many cases, conditions of working appear to be identical, but yet trouble will persist.

Perhaps a point often disregarded, but one which is really of extreme importance is to see that the jig men are trained correctly. After all, carelessness on the part of jiggers may be the biggest set-back ever confronting a dyer. The men handle the cloth and control the dyeing to no small extent. They can make or mar the results. On this account, I do wish to emphasize the necessity of choosing only the best men for jig dyeing, particularly vat dyeing. A jig dyer's job is a stage above that of the ordinary workman and a little extra consideration so far as wage is concerned is often the best policy. Men should be trained to understand that cloth and color cost money and should be handled with respect. A jigger rarely appreciates that a few yards creased at the end of a batch may mean as much to the firm as his wage for the week.

The most important man working for a dyer is his drugman, and a good man here will often make an enormous difference. Accuracy in measuring and weighing out are points never to be neglected. Goods simply will not come up as your pitches if the drug man is not weighing out correctly. In large dyehouses, where several drug men are employed, it is an advantage to try and confine these men to one particular class of colors. Keep one man for blues and greens, and the other say for lighter shades, or divide them out in some sensible manner.

The question of different supplies of water often offers a good excuse for a new dyer when things have all gone wrong.

I have carried out several dyeings using water of 15° hardness and similar dyeings with distilled water, and the results showed that the question of hard water must certainly be considered. In all cases, fuller shades were produced with the soft water, particularly evident in the case of Blue G. C. D. There is I suppose nothing particularly remarkable in these results, due I presume to the action of the caustic soda killing the temporary hardness of the water and at the same time partially destroying some of the dyestuff. Furthermore, using hard water, there is a big tendency to be troubled with stains and scum marks of every description.

If soft water can be obtained, it will give far greater satisfaction in every respect. To correct the hardness with soda ash is the obvious solution, but even here the lime soap formed will always be required to be scummed off before commencing a running. A jigger cannot be wasting about an hour a day doing nothing but scumming the liquor.

Many works now have their own caustic plant and some their own plant for hydrosulfite. These two assistants are to the vat dyer like petrol and oil to the motor mechanic. Obvious though it may seem, it is not always realized that variations can and do occur in these two assistants. Different supplies should be tested and the quantities varied accordingly. Where a tank of caustic is kept in the dyehouse, care must be taken to twaddle regularly. Varying temperature conditions will alone cause surprising fluctuations.

Due to bad stock-keeping, I have seen in many large works cases where time and money have soon been lost. It seems a popular tendency to neglect ordering certain drugs or colors in constant use. The result is one runs out of a standard color and the shades have to be matched up with something fresh. Nothing is more difficult and aggravating at the time. You have a pitch that you know will get the required shade in six ends say, but due to someone's confounded carelessness, you have to start all afresh shading up with a new dyestuff!

It is not long since the vat dyer was given a certain amount of latitude with regard to shade matching. If a shade was fairly near the pattern, it was usually considered good enough. These days are gone now, and our goods must be absolute photographs of what is required. The question arises—Can this be done? I know how many times I have personally asked my manager the question. The answer seems to be that it has got to be done. Trade is such at the moment that goods will be rejected on any excuse whatsoever, and on this account, the most rigid attention must be given to shading. It is often helpful to have someone on the works checking shades after leaving the dyehouse. This need not in any way imply that the dyer himself is incapable of knowing when goods are on shade and when off shade, but merely serves as a double check. Such would often detect any paling off in a batch. The pattern passed by the dyer may be dead on shade and the end piece slightly heavier than the rest of the batch, and so on.

In view of the necessity of absolute perfect match-

ings, it certainly does follow that production will suffer to a certain extent. It is far cheaper to spend a little more time getting the goods right first time than to have same returned as menders.

I prefer to leave untouched the question of actual production figures. Everything depends again on local conditions. Some cloths are dealt with far more easily than others, both from the jiggers' point of view and from that of the dyer. Again, whether it is a question of working standard shades or new matchings enters the problem, the facilities for fetching and removing the cloth, stitching and a hundred and one other little factors. Sufficient is to say that a vat dyer can count every minute of the day booked and then find he has some pitches to mount up in the evening.

In conclusion, I think it will be granted that vat dyeing is one if not the most difficult of all jobs attached to the Trade. The lot of the vat dyer is by no means an easy one. Things are forever going wrong and some unexpected trouble always turning up. One gradually accustoms oneself to the disappointments and set-backs of the game, and after perhaps years of worry and difficulties, begin to realize the enormous scope for developments and improvements, and enter with an even keener enthusiasm.

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## RAYON DYEING AND FINISHING

(Continued from page 712)

(10) Tenter (steam thoroughly on tenter frame before applying maximum width stretch.)
(11) Calender.
(12) Inspect and pack for shipment.

### Taffetas, Lining Cloths and Related Fabrics

The fabrics discussed under this heading are generally scoured on the jig. In some instances the scouring and dyeing operations are simultaneous, in some instance consecutive, and in some instances the fabric is scoured on the jig, dried, and subsequently dyed on the pad machine.

The prime consideration in processing of fabrics of this sort is speed and economy. The constitution of the scouring baths varies from fabric to fabric, and from mill to mill, but they are always so constituted that the desired results can be obtained in a very short time. Generally speaking, the scouring baths used in the jig are much more concentrated than those used for other types of fabric cleansing.

The jig dyeing operation is so well known as to need no further explanation here. The processing of rayon and rayon-containing fabrics on the jig varies from the processing of all-cotton fabrics in only one detail—rayon-containing fabrics should be run as free from tension as possible.

Tension has a very pronounced effect on rayon warp fabrics. Excessive tension accentuates the tendency of these fabrics to show warp streaks or variations from thread to thread within the warp. It has therefore become customary to dye rayon warp fabrics with the least possible degree of tension that will enable the fabric to roll up uniformly on the power beam.

Whenever possible, rayon and rayon-containing fabrics should be dyed on the pad as pad dyeing materially reduces trouble from yarn variations (warp streaks, filling changes, etc.)

The temperature of the padding liquors plays an important part in the results obtained (with respect to the uniformity of the rayon processed). The color box of the pad should be equipped in such a way that the liquor content therein will be maintained at the boil throughout the entire padding operation. This practice allows color to reach the pad and the goods at a working temperature of possible 180 deg. F. (High temperature materially reduces the warp streak of the fabric processed.)

Taffetas and similar fabrics are usually dried on dry cans, although the Palmer machine is resorted to when a specially soft hand is desired. The operation of both dry cans and Palmer's is too well known to need detailed discussion in this series.

The only finishing operation that is customarily applied to taffeta lining cloths, etc., is a back filling operation sometimes given to heavy lining cloths.

### Satins

Satin constructions are so varied that it is difficult to consider these fabrics under a single heading. Some satins, for instance a satin face corset cloth, are handled in the same manner as lining cloths. Other satins, for example the extremely lustrous crepe back satins, would be completely ruined at least from the designer's viewpoint, if finished by lining cloth procedure.

Under the heading of satins, we will consider only those fabrics that need special attention due to the satin construction. The coarser satins can be considered from the dyeing, finishing viewpoint as lining cloths.

Satins are scoured in boil-off tubs in a manner similar to that prescribed for flat crepe fabrics.

The coarser fabrics may be handled in the ordinary reel type machine. The more delicate satins must be handled in full width machines.

While many satin fabrics can be satisfactorily extracted without danger of creasing, etc., some of these fabrics require special extracting procedures. The rotary type of extractor has been found satisfactory for drying the more delicate satins.

Satins are dried on the loop drier, care being taken that the fabric is open to full width before being run into the drier.

As explained under the heading of dyeing, we will not discuss herein the various specialty procedures. The proper finishing of delicate satin fabrics so obviously requires special machinery and special handling that we do not feel free to discuss this subject in detail. It is sufficient to say that the success or failure of satin constructions depends upon the dyeing and finishing procedure used for the same.

(The End)

## THE EVALUATION OF TEXTILE PENETRANTS

(Continued from page 692)

While the apparent greater absorption of water from soap solutions is accounted for at most concentrations on the basis of the greater viscosity of the soap solutions, this explanation does not apply at a concentration of 5 grams per liter. The concentration of soap micelles on the cotton fiber might be advanced as an explanation. However, at concentrations below 1% the soap micelles are very small and it is to be expected that they will not concentrate on the fiber to a greater extent than they are absorbed with the solution during a 15 second contact.

### Penetration of Hard Water Solutions

One of the outstanding advantages of the various penetration assistants as compared with soap is the ability of solutions of the products to effect penetration in hard water solutions under conditions where soap is coagulated. Tests are made of the penetration efficiency of Alkanol B, Gardinol WA Double Powder, and Product D in a solution containing 400 p.p.m. of calcium chloride. This concentration of calcium chloride is above the limit of the hardness of the water ordinarily encountered in industrial practice. A summary of the data obtained is given in Table VII.

**Table VII**

**Solution Retained by Cotton Yarn at 25° C. from Solutions of Textile Assistants in Presence of Calcium Chloride (0.04 g/1)**

| *Conc. g/1* | *Alkanol B* | *Gardinol WA Double Powder* | *Product D* |
|---|---|---|---|
| 0.1 | 25.5% | 29.5% | |
| 0.2 | 31.2 | 33.8 | 22.2% |
| 0.5 | 43.8 | 47.9 | 35.1 |
| 1.0 | 60.5 | 55.6 | 52.5 |
| 2.0 | 76.9 | 75.2 | 66.9 |
| 3.0 | 79.9 | 84.0 | |
| 5.0 | 80.2 | 83.2 | 80.2 |
| 7.5 | | | 84.2 |
| 10.0 | | | 81.1 |

It is evident from a comparison of the data in Tables III and VII that the efficiency of Alkanol B and Product D as penetration assistants is actually increased in calcium chloride solutions as compared with distilled water solutions. On the other hand the efficiency of solutions of Gardinol WA Double Powder decreases slightly under the same conditions. However, the general order of effectiveness remains Gardinol WA Double Powder > Alkanol B > Product D.

### Application to Wool and Silk

The centrifugal method has been applied in this laboratory for the evaluation of the effects obtained by the use of penetration assistants with wool and silk as well as with cotton. The wool skeins used in these tests were prepared from scoured wool yarn (30/2) while the skeins of silk were prepared from Spanish floss silk in the gum (2 ply). The tests were made in distilled water solution at 25°C. A comparison of the data obtained by immersing skeins of cotton, wool, and silk in the gum, in solutions of Gardinol WA Double Powder over a range of concentrations is given in Table VIII.

**Table VIII**

**Water Absorbed by Cotton, Wool and Silk from Solutions of Gardinol WA Double Powder**

| *Conc. g/1* | *Cotton* | *Wool* | *Silk* |
|---|---|---|---|
| 0.0 | 24.0% | 54.4% | 40.0% |
| 0.5 | 52.2 | 52.0 | 45.7 |
| 1.0 | 69.1 | 51.8 | 48.5 |
| 3.0 | 83.6 | 52.7 | 58.8 |

The maximum amount of water retained by boiled-out cotton yarn has been shown to be 90%. Wool yarn, after immersion for 180 seconds in a solution of Gardinol WA Double Powder of 5 grams per liter concentration retains 56% of its weight of moisture while silk in the gum after immersion under similar conditions retains 77% of its weight of water.

The tests summarized in Table VIII show that well-scoured wool wets out readily in water. The results obtained with the silk in the gum are interesting since they show that while the rate of penetration is entirely different from that observed with cotton, a very definite effect can be evaluated by the centrifugal method.

## RELATIONSHIP OF SURFACE TENSION TO THE PENETRATION OF TEXTILE FIBERS

Measurements of the surface tension of solutions of several assistants were made over a range of concentrations in order to determine whether or not a definite relationship can be established between penetration and surface tension. The measurements were made with the du Noüy ring type of tensiometer. The instrument was calibrated against distilled water and the values given in Table IX are corrected on the basis of the calibration. The surface tensions of solutions of Alkanol B, Gardinol WA Double Powder, Gardinol CA Powder, Product D, and soap at 25°C. are given. Each value given in the table represents an average of five experimental determinations.

These data show that the presence of soap, Gardinol WA Double Powder, and Product D produces marked lowering in the surface tension of water. While the surface tensions of Alkanol B solutions are relatively quite low, Alkanol B produces the least effect of the five assistants. These data show that while there is the expected general increase in penetration ability with a decrease in the surface tension there is no general quantitative relationship. For example solutions of Alkanol B at a concentration of 5 grams per liter show a surface tension of 34.1 dynes per centimeter, a value which is higher than that found for solutions of Product D or soap at a concentration of 0.1 gram per liter. However, data obtained by

the centrifugal method (Table III) show that cotton yarn absorbs 83% of its weight of a solution containing 5 grams per liter of Alkanol B while the quantity of liquid absorbed from a solution of soap at a concentration of 0.1 gram per liter is less than 28%. It is evident from this and other comparisons which can be made from the data in Table IX and Table III that there is no quantitative relationship between the surface tension of a solution of a textile assistant and its ability to penetrate textile fibers.

**Table IX**

**Surface Tensions of Solutions of Textile Assistants**

| *Conc. g/1* | *Alkanol B dynes/cm* | *Gardinol WA Double Powder dynes/cm* | *Gardinol CA Powder dynes/cm* | *Product D dynes/cm* | *Soap dynes/cm* |
|---|---|---|---|---|---|
| 0.0 | 72.0 | 72.0 | 72.0 | 72.0 | 72.0 |
| 0.1 | | 43.3 | 41.8 | 33.0 | 33.9 |
| 0.2 | | 33.3 | | 31.5 | 30.6 |
| 0.5 | 51.5 | 28.3 | 35.3 | 31.6 | 26.9 |
| 1.0 | 44.8 | 27.9 | 34.5 | 32.0 | 26.7 |
| 2.0 | | 27.0 | 34.7 | 31.6 | 26.7 |
| 2.5 | 38.2 | | | | |
| 3.0 | | 26.7 | | 31.6 | 26.9 |
| 5.0 | 34.1 | 28.9 | 32.8 | 31.4 | 27.3 |
| 10.0 | 32.6 | | 34.0 | 31.1 | |

## Critical Survey of the Methods Based on Sinking Times

The most satisfactory sinking-time method is that of Draves and Clarkson[2]. Data have been accumulated in this laboratory which make possible a comprehensive comparison between the sinking-time method as developed by Draves and Clarkson and the centrifugal method described in this paper.

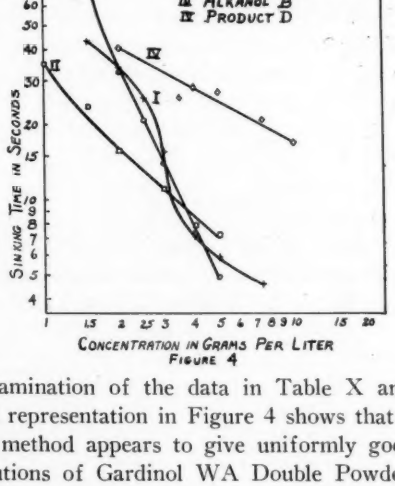
The sinking-time method, as applied by Draves and Clarkson, measures the time required for an aqueous solution of the textile assistant to wet a submerged five gram skein of unbleached cotton yarn to an extent such that its weight plus the weight of absorbed liquid together with that of an attached one and one-half gram sinker will overcome the bouyant force of the wetting solution and cause the skein with its attached weight to sink to the bottom of a cylindrical container. This method can give only a measure of the time required for a textile fiber to reach a certain unknown degree of saturation with a solution containing a known concentration of wetting assistant.

Tests made of the wetting out efficiency at 25° C. of aqueous solutions of Alkanol B, Gardinol WA Double Powder, Product D, and soap by the sinking-time method are summarized in Table X, and a graphical representation of the data is given in Figure 4. Each value given in Table X represents an average of seven experimental determinations, made with skeins of raw cotton yarn (40/2).

**Table X**

**Wetting-out Time of Solutions of Textile Assistants with Cotton Yarn by Sinking-Time Method**

| *Conc. g/1* | *Alkanol B* | *Gardinol WA Double Powder* | *Product D* | *Soap* |
|---|---|---|---|---|
| 1.0 | | 35.0 sec. | | |
| 1.5 | 86.0 sec. | 23.6 | | 43.2 sec. |
| 2.0 | 32.9 | 15.8 | 41.7 sec. | 33.8 |
| 2.5 | 20.9 | | | 25.6 |
| 3.0 | 14.0 | 11.1 | | 15.6 |
| 3.5 | | | 25.9 | |
| 4.0 | 7.4 | 7.9 | 28.4 | 7.1 |
| 5.0 | 4.9 | 7.3 | 27.1 | 5.9 |
| 7.5 | | | 21.0 | 4.6 |
| 10.0 | | | 17.1 | |


I Olive Oil Soap
II Gardinol WA Double Powder
III Alkanol B
IV Product D
Sinking Time in Seconds
Concentration in Grams Per Liter
Figure 4

An examination of the data in Table X and of the graphical representation in Figure 4 shows that the sinking-time method appears to give uniformly good results with solutions of Gardinol WA Double Powder and of Alkanol B, but very erratic results with solutions of soap and of Product D. Very definite experimental difficulties were encountered in observations of the wetting-times of both the soap and the Product D solutions and these difficulties are reflected in the data.

In addition to the wetting tests summarized in Table X, determinations by the same method, relating to the wetting efficiency of Gardinol WA Double Powder at 49° C. were made. The data obtained at 49° C. together with that previously given at 25°C. are summarized in Table XI.

**Table XI**

**Wetting-out at Varying Temperatures of Cotton Yarn in Solutions of Gardinol WA Double Powder by Sinking-Time Method**

| *Conc. g/1* | *Temp. 49°C.* | *Temp. 25°C.* |
|---|---|---|
| 1.0 | 31.5 sec. | 35.0 sec. |
| 1.5 | 15.3 | 23.6 |
| 2.0 | 9.3 | 15.6 |
| 3.0 | 6.2 | 11.1 |
| 4.0 | 5.0 | 7.9 |

The data given in Table XI show that solutions of Gardinol WA Double Powder are considerably more efficient at 49°C. than at 25°C. An examination of the data in Tables III-IV show that this result is in direct contradiction to that obtained with the centrifugal method. A contradiction of this nature is not unexpected for the sinking-time method depends fundamentally upon the tension at the interface liquid-adsorbed gas. It is obvious that this tension is extremely sensitive to variations in temperature. On the other hand the centrifugal method depends basically upon the tension at the interface fiber-liquid and it is this interface that is of fundamental importance in the penetration of the fiber. An examination of the data in Tables III and X adds additional proof that the quantitative evaluation of a penetration assistant by means of the sinking-time method alone may easily give misleading results and lead the investigator to erroneous conclusions. The centrifugal method of testing shows that solutions of soap are considerably superior to those of Alkanol B as penetrating agents in distilled water while the sinking-time method would indicate that solutions of soap are slightly inferior. This discrepancy probably lies in the difficulty of obtaining satisfactory determinations of the wetting-out times in soap solutions by the sinking-time method. The sinking-time method shows that concentrations of 2 grams per liter of Gardinol WA Double Powder and 12 grams per liter of Product D in distilled water solution are required to produce wetting-out of cotton yarn in a 15 second wetting time. This indicates that Gardinol WA Double Powder is six times as efficient as Product D in producing this degree of effectiveness. On the other hand, according to the centrifugal method a concentration of 2.4 grams per liter of Gardinol WA Double Powder produces 82% absorption in cotton yarn during an immersion time of 15 seconds while a concentration of 10 grams per liter of Product D is required to produce the same effect. Gardinol WA Double Powder is only four times as effective as Product D on this basis.

The sinking-time method for the evaluation of wetting agents is quite limited in the range of concentrations over which it may be employed. In the evaluation of agents with which this method has been successfully used the results are erratic when the actual time measured is greater than 40-50 seconds. Thus the lowest concentration of penetration assistant which can be evaluated is approximately 0.1% or 1 gram per liter. However, with many agents of excellent wetting power the method breaks down when the concentration is from 2-3 grams per liter. The sinking-time test cannot be used for a quantitative comparison of the efficiencies of penetration assistants of different types or for the comparison of the relative efficiency at different temperatures. On the other hand the sinking-time method has been found to be decidedly valuable in the standardization of the alkyl-naphthalene sulfonic acid type of penetration assistants. This is largely because slight changes in concentration cause relatively large variations in the sinking time as observed in a logarithmic plot of concentration against sinking time. As a result the actual strength of the wetting assistant present can be determined within an experimental error of five per cent even though the values for the sinking-time may be in error by a considerably greater figure.

### Advantages of Centrifugal Method

The centrifugal method is of value for the comprehensive evaluation and comparison of textile assistants. Evaluations made by this method give a direct measure of the most important factor in the penetration of textile fibers, i.e., a measure of the quantity of a solution absorbed by the fiber. The amount of solution absorbed at the end of any time at any desired concentration of wetting agent can be determined regardless of the degree of saturation which the fiber has reached. The centrifugal method makes possible a determination of the maximum absorption of liquid by a fiber in solutions of all textile assistants. Measurements may be made at any temperature with the assurance that the results obtained are comparable with those obtained at any other temperature. The method can be applied to cotton, wool, or silk fibers.

The technique involved in the use of the centrifugal method can be readily mastered by any person experienced in laboratory methods. The time required for a test compares favorably with the sinking-time method. A series of five individual determinations, required for the determination of the efficiency at a given concentration, may be made in 15-20 minutes. Measurements by the sinking-time method would require from 10 to 20 minutes depending naturally upon the length of the actual sinking-time observed.

### Summary

An improved centrifugal method for the evaluation of textile penetration assistants is described. The advantages of this method as compared with the sinking-time method for the quantitative evaluation of wetting-out agents are pointed out. It is shown that the surface tension of a solution toward air is no criterion of its penetrating ability toward textile fibers. Measurements of the efficiency of a variety of textile assistants as penetrating agents over a range of concentrations and temperatures are given.

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### United Hospital Fund

Mr. Herman A. Metz, president of H. A. Metz & Co., has consented to serve again this year as Chairman of the Drugs, Chemicals and Dyestuffs Auxiliary of the United Hospital Fund appeal.

As it has done for so many years, the Fund will again distribute its income on one basis only—the amount of free service rendered to the poor by each of its fifty-six member hospitals in New York City.

Last year the Drugs, Chemicals and Dyestuffs Auxiliary collected $2,268 for the Fund.

According to Mr. Metz, the free service rendered this year by these hospitals will cost them more than $4,000,000. He is eager to have the men engaged in the drugs, chemical and dyestuffs business unusually well represented this year, both as regards the amount given and the number of contributors.

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### Correction

In the article on the Tube-Tex machine published in our last issue in the sentence beginning "In the processing operation the fabric, preparatory to passing through the machine," etc., the next phrase should read "may be wet or dry in rope or flat form" instead of "weighed or dried in rope or flat form."

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### General Releases

The General Dyestuff Corporation has released cards on the following products:

*Celliton Fast Navy Blue GTN Powder*—said to produce a clearer, fuller shade than the older "GT" brand. It is recommended by the manufacturer for application printing.

*Fast Orange Salt RD*—said to be of interest for print styles on Naphthol AS prepared goods, as well as for discharges and for resist styles. With the Naphthol AS it is said to produce a very bright, reddish orange which the manufacturer claims is exceptionally fast to light, resembling in full shades the fastness of Indanthrens, and which is also said to be exceptional in its fastness to boiling soap.

*Sulphon Navy Blue 2 BN*—an acid color which is chiefly recommended for the dyeing of tin-weighted silk and which gives a clear white discharge with Rongalite.

*Mordant Dyestuff Printed on Cotton Cloth*—Prints of 36 different products in three different strengths are shown.

*Indanthrene Scarlet 4 G Paste*—a new homogeneous product which dyes cotton, viscose and pure silk and said to yield bright yellowish scarlet shades. The dyeings are said to have excellent fastness to light, washing and chlorine, and withstand, if the usual precautions are observed, to the boiling soda chlorine bleach.

Copies of the above circulars may be obtained on request.

## TECHNICAL NOTES FROM FOREIGN SOURCES

### Developed Dyeings

*German Patent No.* 467,059 (4/X/'28)—*I. G. Farben-Ind. A.-G.*—Another extension of the Naphthol AS series. In this case, the first component is a diazotized amino-fluorenone, the process of developing the color being carried out as usual (eight examples). The point emphasized is, that the corresponding pigments in substance are not at all fast to light, while, applied by generation in the fiber, they are surprisingly and extremely fast. The various colors produced are yellow, red, violet, and black.

It seems questionable whether it is not rather an attempt to put a rather useless hydrocarbon, fluorene, to some use, rather than a discovery that the fluorene derivatives are very valuable in the absolute sense.

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### Developed Tris-azo Dyestuffs

*German Patent No.* 469,288 (22/XI/'28)—*I. G. Farben-Ind. A.-G.*—An acidyl-p-diamine, as p-aminoacetanilide, or a p-nitroamine, as p-nitroaniline, is diazotized and coupled to a second component containing an amino-group, as usual, and the amino-azo compound so produced is diazotized and coupled to another second component, an amino-naphthol-sulfonic acid or derivative; and this disazo dyestuff diazotized and coupled to a methyl-ketol, a methyl-phenyl-pyrazolone, etc., the product being then hydrolyzed to set free the acidylated amino group of the original first component, or reduced, if the first component was a p-nitroamine. The products are green dyestuffs, dyeing cotton directly various shades and tones of green, of good fastness to light. They can also be diazotized on the fiber and developed still further to still faster greens, beta-naphthol giving a blackish-green.

Four examples are given.

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